

Advanced Characterization of Molecular Interactions in TALSPEAK-like Separations Systems

Fuel Cycle

Kenneth Nash

Washington State University

In collaboration with:

Argonne National Laboratory

Pacific Northwest National Laboratory

French Alternative Energies and Atomic Energy Commission (CEA)

James Bresee, Federal POC
Bruce Moyer, Technical POC

Final Report

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Principal Investigator: Ken Nash, knash@wsu.edu ph. 509-335-2654

Institution: Washington State University

Collaborators: A Gelis, Argonne National Lab
G. J. Lumetta, S. Sinkov, Pacific Northwest National Lab
C. Marie, CEA Marcoule, France

Student/Postdoc Staff: E. O. Krahn (*Ph.D. student, NMR applications*),
J. Berry (*Ph.D. student, calorimetry applications*)
H. Z. Taylor (*M.S. student, diluent interactions*)
G. Johnson (*M.S. student, graduated 12/2012, calorimetry applications*)
C. Havrilak (*Undergraduate student assistant, NMR/diluent*)
G. Ferru (*Postdoctoral Associate, 50% support, applications of spectroscopic techniques, fast reaction kinetics*)
S. Wahu (*Postdoctoral Associate, 50% support, application of spectroscopic techniques, thermodynamics of TALSPEAK-like systems*)
J. Lapka (*Postdoctoral Associate, 50% support, application of spectroscopic techniques, thermodynamics of TALSPEAK-like systems*)

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2. J. L. Lapka, S. Wahu, K. L. Nash; Ternary Complex Formation and Extraction Modeling in Malonate Buffered Advanced TALSPEAK Separations (*in preparation*)
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4. Cecile Marie, Elizabeth O. Krahn, and Kenneth L. Nash Probing Ligand Exchange Kinetics in Actinide/Lanthanide Solvent Extraction Systems using NMR Spectrometry Proceedings International Solvent Extraction Conference 2014, Wurzburg, Germany, September 7-11, 2014 paper number 4850

5. Kenneth L. Nash, Joseph L. Lapka, Sandrine Wahu, Geoffroy Ferru, Colt R. Heathman, Aaron T. Johnson Improving TALSPEAK Separations: New Knowledge Leading to Alternate Extractants, Holdback Reagents, and Buffers Proceedings of Global 2015 September 20-24, 2015 - Paris (France) Paper 5128
6. Elizabeth O. Krahn and Kenneth L. Nash Insights in Lanthanide-HEH[EHP] Exchange Dynamics in Advanced TALSPEAK Systems Proceedings of Global 2015 September 20-24, 2015 - Paris (France) Paper 5360
7. G. Ferru and K. L. Nash Kinetics of the complexation of lanthanides by DTPA in malonate media in preparation for submission to Dalton Trans.
8. Johnson, Gabriel Eugene, Studies of the Thermodynamics of DTPA Complexation of the Rare Earth Elements at High Ionic Strength: Applications to the TALSPEAK Process, M.S. Thesis, Washington State University, August, 2012.
9. Kenneth L. Nash Advancing the Scientific Basis of Trivalent Actinide-Lanthanide Separations Proceedings Global 2013, Nuclear Energy at a Crossroads, September 29-October 3, 2013, Salt Lake City, Utah, pp. 899-906.

Presentations:

- 1 Joseph Lapka, Ken Nash, Ternary Complex Formation and Extraction Modeling in Malonate Buffered Advanced TALSPEAK Separations, 39th Actinide Separations Conference; 2015 Salt Lake City, UT (talk)
- 2 Cecile Marie, Elizabeth O. Krahn, and Kenneth L. Nash Probing Ligand Exchange Kinetics in Actinide/Lanthanide Solvent Extraction Systems using NMR Spectrometry Proceedings International Solvent Extraction Conference 2014, Wurzburg, Germany, September 7-11, 2014
- 3 Elizabeth O. Krahn and Kenneth L. Nash Insights in Lanthanide-HEH[EHP] Exchange Dynamics in Advanced TALSPEAK Systems Proceedings of Global 2015 September 20-24, 2015 - Paris (France)
- 4 Kenneth L. Nash, Joseph L. Lapka, Sandrine Wahu, Geoffroy Ferru, Colt R. Heathman, Aaron T. Johnson Improving TALSPEAK Separations: New Knowledge Leading to Alternate Extractants, Holdback Reagents, and Buffers Proceedings of Global 2015 September 20-24, 2015 - Paris (France)
- 5 Kenneth L. Nash Advancing the Scientific Basis of Trivalent Actinide-Lanthanide Separations Global 2013, Nuclear Energy at a Crossroads, September 29-October 3, 2013, Salt Lake City, Utah
- 6 K. L. Nash, T. S. Grimes, C. Marie, D. Brigham, G. Johnson, K. Uruga, M. Nilsson, Teasing Out the Details of TALSPEAK Separations Using Multiple Modes of Analysis, 245th American Chemical Society Meeting and Exposition, New Orleans, LA April 7-11, 2013
- 7 A.T. Johnson, K. L. Nash Study of the Interaction Between Cyanex-923 and Cyanex-272, HEH[EHP] and HDEHP, 245th American Chemical Society Meeting and Exposition, New Orleans, LA April 7-11, 2013

- 8 Kenneth L. Nash, Colt R. Heathman, Aaron T. Johnson (and others) Minor Actinide Separation Research at WSU: New Insights, New Systems, New Reagents DOE – NE Fuel Cycle R&D Working Group meeting, Albuquerque, NM, April 2-4, 2013
- 9 J. Lapka, S. Wahu, K. Nash, Development of a malonate buffer system for use in advanced TALSPEAK separations. 248th National ACS meeting, August 10-14, 2014, San Francisco, CA 86
- 10 E. O. Krahn, K. L. Nash, Probing ligand exchange reactions of lanthanide HEH[EHP] complexes in organic solvents using ³¹P NMR spectroscopy 248th National ACS meeting, August 10-14, 2014, San Francisco, CA NUCL 88
- 11 Kenneth L. Nash, Joseph L. Lapka, Geoffroy Ferru, Colt R. Heathman, Aaron T. Johnson Improving TALSPEAK Separations: Potential Impacts of Alternate Extractants, Holdback Reagents, Buffers, and New Knowledge. 18th Separation Science and Technology for Energy Applications Conference, October 27-30, 2014, Oak Ridge, TN
- 12 Kenneth L. Nash, Jenifer C. Braley, Derek M. Brigham, Travis S. Grimes, Colt R. Heathman, Aaron T. Johnson, Joseph L. Lapka, Mikael A. Nilsson, Cecile Marie New Options to Improve TALSPEAK-Based Separations of Trivalent Actinides and Lanthanides Methods & Applications of Radioanalytical Chemistry (MARC) X, April 12-17, 2015, Kailua-Kona, Hawaii

Purpose: Combining unit operations in advanced aqueous reprocessing schemes brings obvious process compactness advantages, but at the same time greater complexity in process design and operation. Unraveling these interactions requires increasingly sophisticated analytical tools and unique approaches for adequate analysis and characterization that probe molecular scale interactions. Conventional slope analysis methods of solvent extraction are too indirect to provide much insight into such interactions. This project proposed the development and verification of several analytical tools based on studies of TALSPEAK-like aqueous processes. As such, the chemistry of trivalent fission product lanthanides, americium, curium, plutonium, neptunium and uranium figure prominently in these studies. As the project was executed, the primary focus fell upon the chemistry of trivalent lanthanides and actinides.

The intent of the investigation was to compare and contrast the results from these various complementary techniques/studies to provide a stronger basis for predicting the performance of extractant/diluent mixtures as media for metal ion separations. As many/most of these techniques require the presence of metal ions at elevated concentrations, it was expected that these studies would take this investigation into the realm of patterns of supramolecular organization of metal complexes and extractants in concentrated aqueous/organic media. We expected to advance knowledge of the processes that enable and limit solvent extraction reactions as a result of the application of fundamental chemical principles to explaining interactions in complex media.

Project Objectives:

- Develop and extend previous applications of NMR spectroscopy to the characterization of metal extractant interactions in solvent extraction

- Develop entropy titration calorimetry as a thermochemistry characterization tool for solvent extraction relevant systems
- Through application of optical spectroscopy techniques and complementary physicochemical analysis methods, characterize metal complex interactions in solvent extraction systems

Logical Path: This program focused on development of new analytical methods as three parallel thrust areas: spectroscopic characterization methods, thermochemical methods, and various physicochemical characterization methods, emphasizing optical spectroscopy, as molecule/ion-specific methods for characterizing the chemistry of solvent extraction systems. The focus on f-element chemistry facilitates several of these applications, but these species are most critical components for the development of advanced separation procedures, so are appropriately featured in the research program. Where appropriate, we sought to complement the experimental program with computational modeling (thermodynamic models and molecular-scale computations using molecular mechanics/molecular dynamics/quantum mechanics approaches). Development of these tools proceeds as fundamentally independent activities designed to serve as the framework for graduate student Ph.D. thesis projects.

The project organization was such that weekly research group meetings were held with all members of this research team and the remaining members of the research group present. In addition, our research team interaction is such that frequent ad hoc one-on-one meetings are held, almost on a daily basis. The methods targeted for development provide complementary information, thus it is expected that the parallel observations should support the creation of more efficient processes. The cross-cutting weekly group meetings regularly inspire the cross fertilization of ideas between the several different projects active in the research group. For example, work funded by the FCR&D Sigma Team for Minor Actinide Separations program has provided the first important test system for the development of fluorescence emission spectroscopy applications. It was expected that by year three of this program the methods developed would be used in a complementary fashion to support new separation system design. The ultimate focus is on providing a foundation on which to build new separations methods. This objective was achieved, as the methods employed did in fact provide useful insights into the description of a malonate-based Advanced TALSPEAK process option and for the characterization of the TALSPEAK-MME combined extractant system (funded separately but benefitting from the insights gained in this program). Each of these systems also was supported by the Sigma Team for Minor Actinide Separations project.

Outcomes: Primary expected outcome was the development of advanced characterization tools for solvent extraction separations that are relevant to advanced nuclear fuel cycles. These unconventional tools (more correctly, conventional tools not typically utilized in separation science) address molecular scale interactions in solvent extraction systems at a level of detail not commonly practiced. The payoff is in the development of more robust separation systems that perform predictably. As with all graduate education activities, an equally important outcome will be the human capital of trained scientists with specific knowledge relevant to sustained innovation in nuclear fuel cycle research and development. Much of the research conducted in this program focuses on TALSPEAK-like applications in which trivalent actinides are selectively retained in the aqueous phase while lanthanides are extracted. Where appropriate, we also examined the chemistry of uranium, neptunium, and plutonium for their intrinsic interest, their

relevance to advanced fuel cycle development, and to give young investigators an opportunity to work hands-on with these actinides, arguably the most interesting elements of the periodic table.

Results: For reporting purposes, this program has been broken down into three separate tasks, as the following structure attests. Students and postdocs are always encouraged to act independently, but to seek advice as needed from the PI, national lab partners, and colleagues. As is true of all research, productivity always increases geometrically (sometimes exponentially) with knowledge. With young investigators their limited experience often results in comparatively low productivity that inevitably increases with the mistakes made along the way.

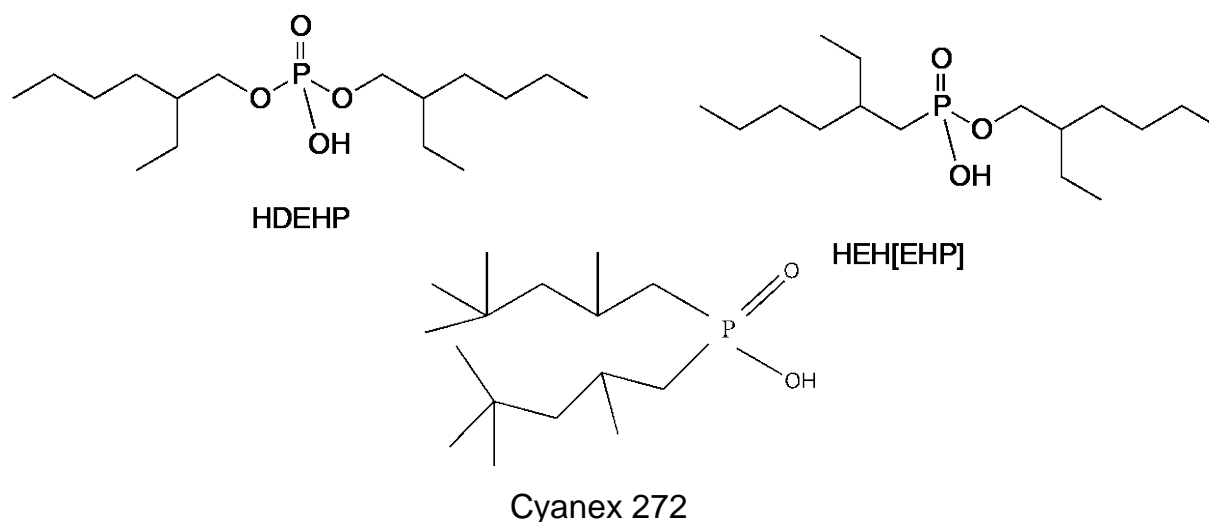
Task 1. Development of NMR Spectroscopic Methods for Lanthanide/ Actinide Partitioning:

This research thrust has its roots in work done by former WSU posdoc, Dr. Cecile Marie, presently a Research Engineer at the CEA Marcoule, Atalante facility and a co-investigator/consultant on this project. The grad student assigned to this portion of the project (Krahn) is an experienced research practitioner, having previously worked as an M.S. level technician at Argonne National Lab. She returned to graduate school with the purpose of getting a Ph.D. and ultimately returning to ANL with increased responsibilities. Because of this prior experience, she has been assigned the most challenging of the three tasks, development of NMR spectroscopy as a characterization tool. Following the work of Dr. Marie, Krahn started her investigation with a confirmation of some of the previous work, examining the rate of exchange of HDEHP on $\text{La}(\text{DEHP} \cdot \text{HDEHP})_3$ and $\text{Sm}(\text{DEHP} \cdot \text{HDEHP})_3$ in 1,3-diisopropyl benzene. The agreement was found to be adequate to move on to characterization of the interaction of the Advanced TALSPEAK extractant $\text{HEH}[\text{EHP}]$, a phosphonic acid structural analog of HDEHP. La^{3+} and Sm^{3+} were again selected for analysis due to their absent/negligible magnetic moments, which greatly simplifies the interpretation of the experiments. Ligand exchange dynamics were found to be similar to those of HDEHP, but not identical. Likewise, investigation of heavier diamagnetic rare earths Y^{3+} and Lu^{3+} established that these metal ions form “substitution-inert” complexes (on the NMR time scale), as was reported for HDEHP. These heavy lanthanide complexes in the $\text{HEH}[\text{EHP}]$ system are characterized as showing evidence for multiple phosphorus environments in these complexes, an unexpected result indicating some otherwise undetectable complexity in the coordination chemistry. Some initial work also addressed the interactions of lanthanide ions with the phosphinic acid extractant Cyanex 272. In this case also, distinct differences were seen in the spectral features of Sm^{3+} and Lu^{3+} complexes. However, following some preliminary results that revealed unexpected complexity in the ^{31}P spectra, these studies were shelved with an enhanced focus on diluents effects in $\text{HEH}[\text{EHP}]$ extraction systems that are relevant to Advanced TALSPEAK and ALSEP separation systems.

To give Ms. Krahn an opportunity to attain a stronger understanding of the power (and limitations) of NMR spectroscopy, she spent 10 weeks during the summer, 2013 at Argonne (at no expense to this project) learning NMR methodology and techniques with expert NMR spectroscopist Dr. John Muntean (a former collaborator with the PI). This experience greatly expanded Krahn's confidence, competence, and sophistication in experimental design. Krahn successfully completed her oral preliminary examination to become officially a Ph.D. candidate. During the academic year that began in August 2014, Krahn relocated to Argonne National Lab, where her day-to-day activities were guided by co-investigator Gelis. Having established a relationship with Dr. Muntean, it was expected that he would continue to mentor her development as a physical scientist and an NMR spectroscopist. Though the focus remained

throughout on HEH[EHP] exchange dynamics, various diluents, phase modifiers, and co-extractants (e.g., tetraoctyldiglycolamide, TODGA) interactions were also investigated. The several observations that are described below represent some of the more mature conclusions that have been drawn from these studies; other observations are still under discussion and debate and so inappropriate for detailed discussion at present. We expect that this research will ultimately generate as many as six important new publications, many focusing on illumination of solvent-solute effects in solvent extraction.

We have also begun an examination of the influence of entrained water in the extractant phase and have also done some preliminary investigations (and experimental design exercises) on application of NMR methods to the characterization of mixed extractant solutions in connection with our Sigma Team research. Such studies are integrally responsive to advanced separations trends for combined extraction processes and address unknown aspects of other projects in progress in our research. The structures of the three extractants investigated so far are shown below.



Ligand exchange reactions, probed through NMR spectroscopy, probe an important step in complex formation reactions. Studying these reactions can lead to better understanding of the interactions of the metal ions and molecules involved in these reactions. This technique has less often been applied to understand interactions of bulkier ligands with cations in the apolar phase of solvent extraction systems. One such study by Marie *et al.*, found that the ligand exchange of the phosphoric acid TALSPEAK extractant, HDEHP, in equilibrium with La^{3+} was 25 times faster than its exchange with Sm^{3+} .¹ Based on the activation parameters, the exchange mechanism on La^{3+} was seen to proceed via a dissociative interchange mechanism, which presumes an expansion of the primary coordination sphere of the La^{3+} cation. For the more strongly bound Sm^{3+} , activation parameters point to a shift to an associative mechanism. Based on the Marie *et al.* study, the less acidic phosphonic acid suggested for used in advanced TALSPEAK processes, HEH[EHP], was studied. In the HEH[EHP] system, slower exchange on

¹ Marie C, Hiscox B and Nash KL, *Dalton Transactions*, **41**, 1054 (2012).

La^{3+} and Sm^{3+} is observed correlating with stronger bonding interaction with the more basic O-donor atoms of the phosphonic acid.² While HEH[EHP] exchange on Sm^{3+} also proceeds via an associative mechanism, the exchange on La^{3+} has more associative character than its counterpart in the HDEHP system.

Continuing studies are investigating the effect that changing the concentration of the free ligand has on the ligand exchange rate constants and mechanisms in the aromatic diluent, 1,3-diisopropylbenzene (1,3-dipb). Variable temperature NMR spectra were collected on different samples with varied $[\text{HEH}[\text{EHP}]]_{\text{free}}$ in equilibrium with La^{3+} . Complete band shape analysis was performed on the

experimental data and used to generate an Eyring plot (Figure 1.1). Comparing the different $[\text{HEH}[\text{EHP}]]_{\text{free}}$ investigated, at room temperature, the more free HEH[EHP] in the solution, the faster the exchange can occur (Figure 1.2). From the Eyring plot, the activation enthalpy and entropy for each environment can be determined (Table 1.1). This data suggests that when there is an increase in free ligand in the surroundings of the coordinated metal center, the exchange proceeds via an interchange mechanism with some dissociative character. However, as the concentration of free ligand decreases, there is a shift to a mechanism with more associative-like character. There also appears to be a shift from about seven HEH[EHP] molecules associating with the metal center to about six molecules, respectively. Further experiments varying $[\text{HEH}(\text{EHP})]_{\text{free}}$ will be undertaken with La^{3+} and then switching to Sm^{3+} in an effort to resolve the mechanistic implications of the pattern observed.

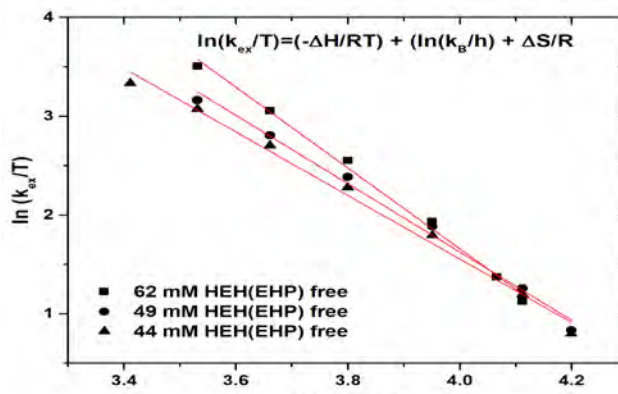


Figure 1.1. Eyring plot for $[\text{HEH}(\text{EHP})]_{\text{free}}$.

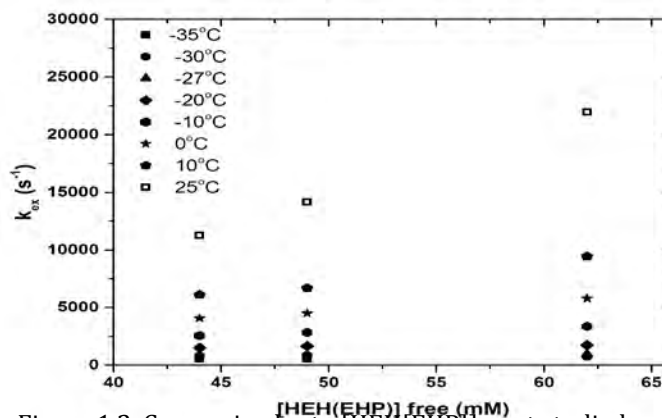


Figure 1.2. Comparing k_{ex} to $[\text{HEH}(\text{EHP})]_{\text{free}}$ at studied temperatures.

The next portion of this study focused on investigating the effect that changing the diluent from 1,3-dipb to an aliphatic diluent, *n*-octane, has on the exchange rate (Figure 1.3, Table 1.1). The data suggests that at room temperature the exchange is occurring about twice as fast in octane as it did in 1,3-dipb. However, the interpretation of this result is complicated by the knowledge that ratio of free ligand to bound is different in the experiments. Based on the influence of free

² Krahn EO, Marie C and Nash KL, *Proceedings of the International Solvent Extraction Conference*, 2014.

ligand concentration, it is difficult to make a direct comparison between the sets of data. Continued studies are planned in *n*-octane while varying the $[\text{HEH}[\text{EHP}]]_{\text{free}}$.

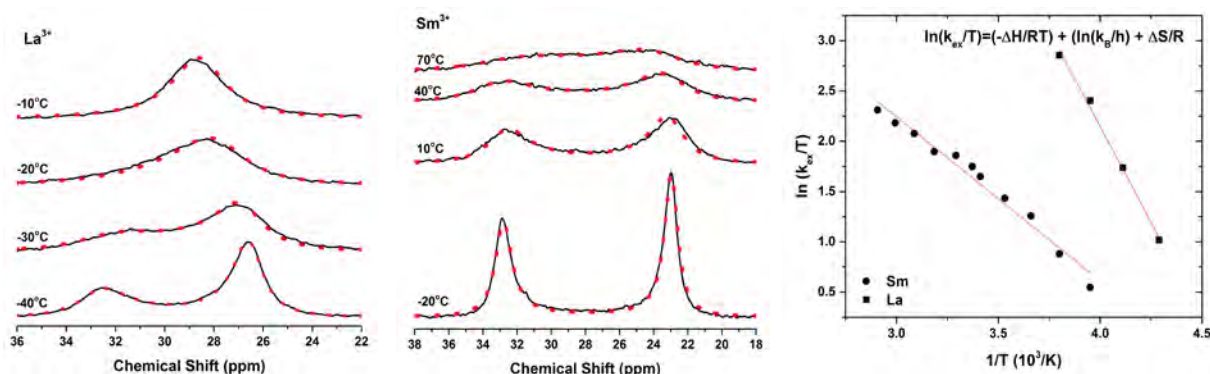


Figure 1.3. Representative variable temperature ^{31}P NMR experimental (solid) and calculated (dots) spectra of HEH[EHP] exchange on La^{3+} (left) or Sm^{3+} (middle) and the Eyring plot generated from the rate constants (k_{ex}) determined through complete band shape analysis (right).

Table 1.1. Activation parameters for 0.1 mol L⁻¹ HEH[EHP] in equilibrium with Ln^{3+} .

Diluent	Ln^{3+}	$[\text{Ln}^{3+}]_{\text{org}}$ mmol L ⁻¹	$[\text{HEH}[\text{EHP}]]_{\text{free}}$ mmol L ⁻¹	k_{ex} @ 25°C s ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ K ⁻¹	HEH[EHP] to Ln^{3+}
1,3-dipb	La^{3+}	5.5±0.3	62	2.20(±0.07)×10 ⁴	40.0±1.2	-48±5	7.2±0.3
1,3-dipb	La^{3+}	8.6±0.1	49	1.41(±0.06)×10 ⁴	28.7±1.3	-69±5	6.2±0.1
1,3-dipb	La^{3+}	9.1±0.1	44	1.13(±0.05)×10 ⁴	26.7±1.1	-78±4	6.3±0.1
<i>n</i> -octane	La^{3+}	9.1±0.1	40	3.0(±0.1)×10 ⁴	31.7±1.5	-53±6	7.1±0.1
<i>n</i> -octane	Sm^{3+}	8.3±0.1	48	1.6(±0.1)×10 ³	13.5±0.7	-138±3	7.0±0.1

The present technique can probe exchange on the lighter lanthanides because it occurs on the NMR time scale. The heavier lanthanides are substitution inert on this time scale, hence NMR spectroscopy is not a suitable technique for determining the ligand exchange rate in these systems. We do know that the conventional TALSPEAK system suffers from slow phase transfer kinetics for lanthanides heavier than Nd in the absence of lactate. It has generally been considered that the slow rate of extraction in TALSPEAK for heavy lanthanides is governed by the rate of release of the cation by DTPA, but these results suggest that the slowed ligand exchange for lanthanide HDEHP complexes might also contribute to the slow extraction of heavy lanthanides.

To explore the potential influence of a phase modifier on extractant exchange dynamics, a system with a more polar diluent was investigated, specifically introducing 1-octanol as a co-solvent with *n*-octane. Room temperature NMR spectra suggest that the addition of 1-octanol,

up to 10%, increases the rate of exchange (Figure 1.4). This is most evident with HEH[EHP] exchange on Sm^{3+} . With no 1-octanol in the system, there are two not completely resolved peaks representative of slow exchange (on the NMR time scale). Upon addition of 10% 1-octanol, there is a single peak representative of fast exchange between the free and metal-coordinated ligand. These data offer a promising system to investigate the heavier lanthanides, however, it also adds an additional component to the system. It is necessary to understand if 1-octanol is interacting with HEH[EHP] or the cation. The path forward clearly includes several options. The path taken will be dictated by the emerging results, as must be the case in exploratory chemistry research.

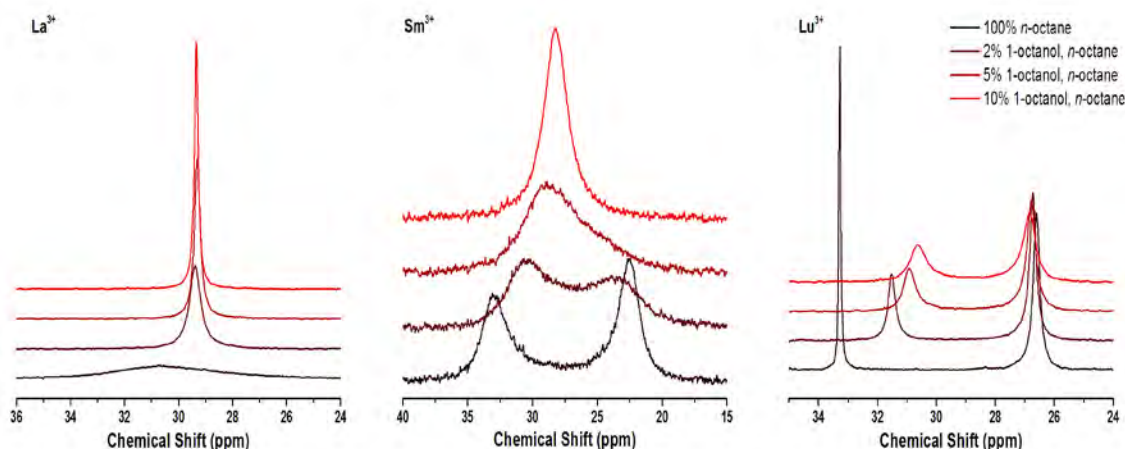


Figure 1.4. Room temperature ^{31}P NMR spectra of 0.1 mol L^{-1} HEH[EHP] in equilibrium with La^{3+} (left), Sm^{3+} (middle) or Lu^{3+} (right) in vary concentrations of 1-octanol in *n*-octane.

Despite conclusion of the funding supporting this project, Krahn continues to examine ligand exchange dynamics features of HEH[EHP] (phosphonic acid extractant central to Advanced TALSPEAK process) with La, Sm, Y, Lu in 1,3-di(isopropyl)benzene media. As noted above, La^{3+} and Sm^{3+} exchange dynamics are measurable using NMR spectroscopy and slower than comparable rates for HDEHP reported previously; rates may ultimately prove to be dependent on extractant concentration - investigation continues. The mechanistic details are still incompletely understood. Ligand exchange on Y^{3+} and Lu^{3+} is slow under all accessible temperature conditions, but may be measurable in mixed diluent media containing 1-octanol phase modifier. ^{31}P NMR spectra indicate Y complex environment composed of a single M-HEH[EHP] complex (one ^{31}P peak), presumed to be the conventional "tris-dimer". Lu complexes indicate more complex stoichiometry including the possibility of multiple phosphorus environments in the complex. Planned phosphinic acid studies (Cyanex 272) were postponed to permit focus on HEH[EHP]. Introduction of co-solvent 1-octanol (1-30% mole % relative to the diluent) as a polar phase modifier dramatically increases the rates of ligand exchange accompanied by a shift in peak positions, perhaps indicating a shift from dimer to monomer ligand speciation.

To advance our work being conducted under our Sigma Team for Minor Actinides project, we have applied the ^{31}P NMR spectroscopy methods to characterize the nature of the interaction between HEH[EHP] and Cyanex 923 in dodecane. Based on these experiments and parallel optical spectroscopy measurements, a model for interaction between the extractants and for mixed-ligand complexes has been developed and a manuscript describing the results is in an advanced stage of preparation. While she was at Argonne National Lab, Ms. Krahn, working under the day-to-day supervision of Project partner Gelis and NMR spectroscopist Muntean,

conducted investigations of HEH[EHP] ligand exchange dynamics in mixed media. The studies of mixed extractant systems and phase modifiers are integrally responsive to advanced separations trends for combined extraction processes and address unknown aspects of other projects in progress in our research. The strategic intent of this work is to advance the utility of advanced spectroscopic techniques in nuclear applications of applied separations science. A brief manuscript describing features of the above described work has been published in the proceedings of ISEC 2014 and another at the Global 2015 conference. The general features of that investigation are described below.

Summary – *Nuclear magnetic resonance (NMR) spectroscopy is recognized as a technique that could provide useful insights into ligand exchange reaction dynamics in the apolar organic phase; application of NMR spectroscopy is the principle focus of this work. The results of a ligand exchange study for (2-ethylhexyl) phosphonic acid mono (2-ethylhexyl) ester (HEH[EHP]) interactions with lanthanides ions in an aromatic diluent are presented. Through collection of NMR spectra at variable temperatures, exchange rate constants and activation parameters can be calculated. This approach provides insight into the mechanism of HEH[EHP] exchange. Varying the concentration of free HEH[EHP] in the reaction aids in the determination of the rate law. Additional information on the dynamics of complex formation can be ascertained by changing the diluent.*

INTRODUCTION

Closed, or partially closed, nuclear fuel cycles seek to isolate individual useful or troublesome elements (or groups of elements) from the complex mixture that is dissolved used nuclear fuel. Closed fuel cycles supporting actinide transmutation have the challenging step of separating trivalent actinides from trivalent lanthanides, which are neutron poisons. In the conventional TALSPEAK (Trivalent Actinide-Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes) process, solvent extraction methods are employed to partition the lanthanides and actinides between an organic phase, containing an organophosphorus extractant, and an aqueous phase containing a concentrated lactic acid buffer and actinide-selective aminopolycarboxylate complexing agent. While previous studies have focused on the application and development of the TALSPEAK process, including a engineering scale demonstration of the process, recent years have shown an increase in studies into the fundamental chemistry involved in the process. Recent studies into advanced TALSPEAK processes have investigated alternatives to the strong extractant molecules and complexing agents used in the conventional TALSPEAK process, to alleviate some of the drawbacks of the process: stringent pH range and slow phase transfer kinetics, to mention a couple. Also, the time required for process design and optimization could be greatly reduced by increased knowledge of the fundamental chemistry of these systems.

Of interest in this study are the rate and mechanism of complex formation in the organic phase between bulky extractant molecules and the extracted metal. Surprisingly little information is found in the prior literature focusing on the dynamics of metal-extractant interactions in such systems. Of the literature available, the majority of studies have focused on solvating extractant

molecules – with only a handful investigating exchange dynamics of cation exchanging ligands, like those extractant molecules used in TALSPEAK-like systems.^{1,2} Such dynamic ligand exchange reactions constitute an important subset of chemical reactions. The exchange reactions represent a system in equilibrium where there is no net chemical change, yet a reaction occurs. Such a reaction involves a solvent molecule coordinated to a metal, moving to the bulk, and being replaced by another solvent molecule from the bulk. These reactions can be classified as dissociative, formation of a lower coordination number intermediate, associative, formation of a higher coordination number intermediate, or interchange, classified with a formation of an outer-sphere complex intermediate.

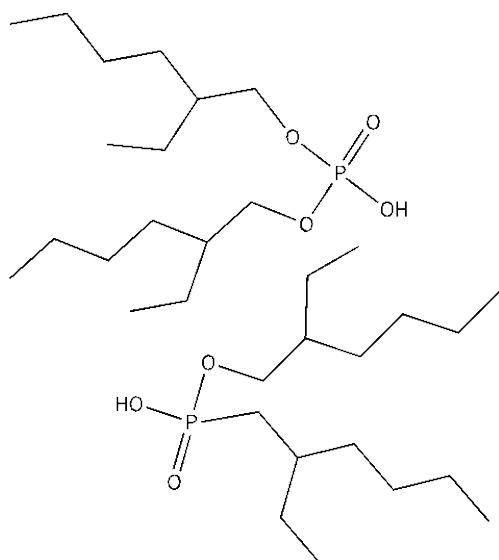
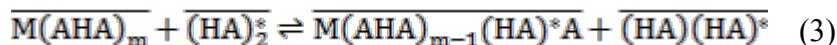
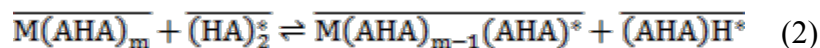


Figure 1.5. HDEHP (top) and HEH[EHP] (bottom)

Cation exchanging ligands extract the cation, Ln(III), into the organic phase by releasing three protons into the aqueous phase as shown in the extraction equilibrium in equation 1.³



Di-2-ethylhexylphosphoric acid (HDEHP, Figure 1.5) is the cation exchanging extractant used in the TALSPEAK process.³ HDEHP exists predominately as dimers in apolar organic media, like most cation exchanging extractants.⁴ Three of these dimers coordinate to the Ln³⁺ cation in the organic phase.⁵ An interesting question is whether dimers remain intact during ligand exchange in the organic phase, represented by equation 2, or a single monomer is exchanging on the metal center, equation 3.



The binary complexes that form in the organic phase, Ln(AHA)₃ (Ln = La or Sm), have been studied by Marie *et al*.¹ the rate data presented in the study found that there was faster exchange for La(AHA)₃ than Sm(AHA)₃. The activation parameters suggest that the reaction proceeds via a dissociative interchange mechanism for La³⁺, whereas for Sm³⁺ it proceeds via an associative mechanism. A few suggestions were offered to explain this difference in mechanism. First, the Sm ion is a smaller, harder Lewis acid which would experience stronger bonding interactions with the O-donor atoms of the HDEHP dimer. Another explanation proposed is that in the La(AHA)₃ complex HDEHP dimers are being exchanged, while in the Sm(AHA)₃ complex HDEHP monomers are being exchanged due to the stronger interactions.

The more basic phosphonic acid analog of HDEHP, (2-ethylhexyl) phosphonic acid mono (2-ethylhexyl) ester (HEH[EHP], Figure 1.5), has been suggested for use in advanced

³ AHA⁻ represents the deprotonated form of the HDEHP dimer (HDEHP·DEHP) or HEH[EHP] dimer (HEH[EHP]·EH[EHP]). The species with a line over the top represents a species in the organic phase.

TALSPEAK processes.⁶ HEH[EHP] exchange studies could offer insight into how changing basicity affects complex formation in the organic phase. Initial studies into HEH[EHP] exchange on a Ln^{3+} center ($\text{Ln}^{3+} = \text{La}^{3+}$ or Sm^{3+}) were performed in 1,3-dipb so that an easy comparison could be made with the HDEHP system previously studied by Marie *et al.*¹ These initial data showed that HEH[EHP] exchange on La^{3+} was ten times slower than HDEHP exchange on La^{3+} .⁷ There was also a shift from exchange via a dissociative interchange mechanism, in the case of HDEHP, to an interchange mechanism with more associative character. For exchange on the Sm^{3+} center, the exchange was slightly slower for HEH[EHP] than HDEHP with comparable activation parameters, suggesting the exchange proceeded via an associative mechanism in both systems. This demonstrated that, for the presented data set, the stronger electrostatic interactions correlated with a decrease in ligand exchange rate ($k_{\text{La:HDEHP}} > k_{\text{La:HEH[EHP]}} > k_{\text{Sm:HDEHP}} > k_{\text{Sm:HEH[EHP]}}$).⁷ In the present study, the HEH[EHP] exchange data is extended by altering the organic phase conditions to further elucidate an exchange mechanism.

II. EXPERIMENTAL

II.A. Materials

HEH[EHP] was purchased from Yick-Vic Chemicals and Pharmaceuticals Ltd. and purified to > 99% using the third phase formation procedure.⁸ The purity was verified using ^{31}P NMR spectrometry. The diluents 1,3-diisopropylbenzene (1,3-dipb), octane, and 1-octanol were purchased from Sigma-Aldrich and used as received. The lanthanide nitrate stock solutions were prepared from lanthanide oxides (99.9999%) purchased from Arris International and standardized for metal, nitrate and H^+ concentrations.

II.B. Preparation of organic solutions

To prepare the extracted complex samples, aqueous lanthanide nitrate solutions containing various amount of metal ($5 - 15 \text{ mmol L}^{-1}$) were contacted by vortex mixing for 20 minutes with organic solutions containing 0.1 mol L^{-1} HEH[EHP] in various diluents. The samples were centrifuged for 10 minutes and the two phases were carefully separated after centrifugation. The organic phase was used directly for ^{31}P NMR studies. The metal concentration in the aqueous phase was determined before ($[\text{Ln}^{3+}]_{\text{aq, init}}$) and after extraction ($[\text{Ln}^{3+}]_{\text{aq, eq}}$) using a buffered arsenazo solution to complex the metal, based on a previously reported method.⁹ UV-Vis spectra were taken of the solutions and compared to those of known concentration. These were performed in triplicate to determine the concentration of lanthanide in the organic phase ($[\text{Ln}^{3+}]_{\text{org}} = [\text{Ln}^{3+}]_{\text{aq, init}} - [\text{Ln}^{3+}]_{\text{aq, eq}}$).

II.C. ^{31}P NMR experiments

The ^{31}P NMR spectra were collected on a Bruker 500 MHz Avance III Spectrometer with a 5 mm broadband probe. The ^{31}P NMR experiments were performed at 202 MHz with gated proton decoupling. The ^{31}P 90° pulse was calibrated to be $11 \mu\text{s}$ and a relaxation delay of 10 s was used. The metal loaded organic phases were analyzed using a 5 mm NMR tube. A coaxial insert was filled with acetone- d_6 (99.9 atom-% D) as the lock solvent for low temperature work ($< 25^\circ\text{C}$), and DMSO- d_6 (99.9 atom-% D) as the lock solvent for high temperature work ($> 25^\circ\text{C}$). A

chemical shift reference of 0.1 mol L⁻¹ phosphoric acid (Fisher Chemicals, 85%) was used for room temperature spectra. The variable temperature was calibrated by ¹H NMR spectroscopy of methanol (< 20°C) or ethylene glycol (> 20°C) at the same gas flow rate as the experiments. For collection of variable temperature NMR spectra for the La³⁺ systems, the temperature was varied anywhere from -45°C up to 20°C. For the Sm³⁺ system, spectra were collected between -10°C up to 80°C.

III. THEORY

Collection of ³¹P NMR spectra of HEH[EHP] in equilibrium with Ln³⁺ (Ln³⁺ either La³⁺ or Sm³⁺) ions at different temperatures allows the application of Complete Band Shape (CBS) analysis to determine the rate constants at different temperatures. CBS analysis is based on Rogers and Woodbrey's general equations for an uncoupled two-site exchange.¹⁰ Representative ³¹P NMR spectra collected at different temperatures are shown in Figure 1.6, with the slow exchange between bulk and coordinated ligand represented by two distinct peaks (bottom spectrum) and the fast exchange represented by a single broad peak (top spectrum). The data was fit to the CBS equation using Origin Pro 9.1 to determine the mean lifetime of the nuclei (ligand) in its metal-coordinated form (χ). To determine the exchange rate constant, k_{ex} , χ is set equal to the fractional populations of the nuclei in the free state (p_A) over k_{ex} ($\chi = p_A/k_{ex}$).

The generation of an Eyring plot, natural log of k_{ex}/T versus $1/T$ (with temperature in K), can be used to determine the activation parameters of the reaction, the enthalpy of activation (ΔH^\ddagger) and the entropy of activation (ΔS^\ddagger). These parameters can aid in assigning a mechanism to the dynamic exchange reaction, suggesting whether it is dissociative, associative or interchange.

High enthalpy of activation (ΔH^\ddagger greater than about 25 kJ mol⁻¹) and positive entropy of activation suggest the rate-limiting step is the stretching or breaking of the metal-ligand bond forming a lower coordination number intermediate, representative of a *dissociative* mechanism. Low enthalpy of activation (ΔH^\ddagger less than about 25 kJ mol⁻¹) and very negative entropy of activation provides information correlated to an *associative* mechanism where the formation of metal ligand bond and a higher coordination number intermediate is the rate-limiting step. The *interchange* mechanism represents one that is essentially in-between the previously discussed mechanisms, with weak bonding to both the entering and leaving group and could include the formation of an outer-sphere complex.

Assigning these mechanisms to the dynamic exchange reactions continues to add valuable information to understanding complex formation.¹¹

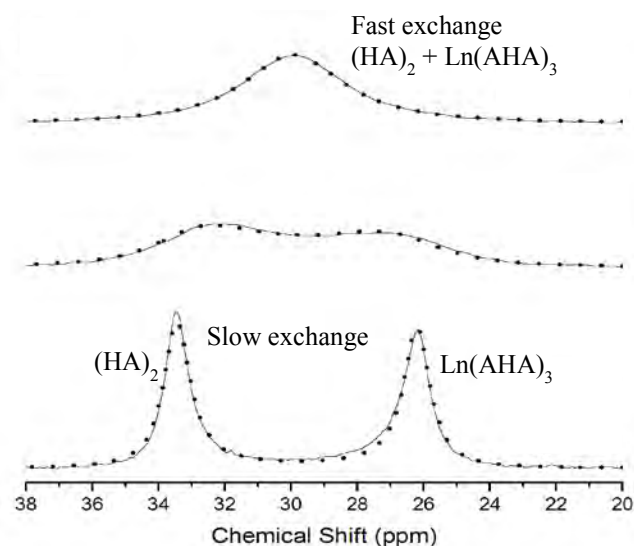


Figure 1.6. Variable temperature ³¹P NMR spectra; the bottom spectrum represents the slow exchange region; the top spectrum represents the fast exchange region. The dotted lines represent the CBS analysis for the respective spectrum.

IV. RESULTS

IV.A. Suggested mechanism of HEH[EHP] exchange on La(AHA)₃ complexes in 1,3-dipb

Building on the previous studies investigating HDEHP or HEH[EHP] exchange,^{1,7} the ratio of bulk to coordinated HEH[EHP] was varied. Collecting this data can aide in the assignment of a rate law leading to a more complete understanding of the mechanism of exchange in the organic phase. Towards this end, the amount of Ln³⁺ in the aqueous phase was varied and extracted into 0.1 mol L⁻¹ HEH[EHP] to change the amount of free ligand in the organic phase. Variable temperature NMR spectra were collected for each concentration and CBS analysis was performed to determine the rate constant at the temperatures. Through application of the Eyring relationship, the rate constant at 25°C was determined along with the ΔH^\ddagger and ΔS^\ddagger .

The Eyring plot for HEH[EHP] exchange on La(AHA)₃ complexes in 1,3-dipb with variable amounts of free HEH[EHP] (Figure 1.7, solid symbols) was used to determine the activation parameters for the five reactions studied (ΔH^\ddagger and ΔS^\ddagger , Table 1.2). As the concentration of free ligand increases, the exchange rate constant at 25°C increases by almost an order of magnitude from the lowest (31 mmol L⁻¹) to the highest (63 mmol L⁻¹) concentration of free HEH[EHP]. Furthermore, the activation parameters shift, ΔH^\ddagger and ΔS^\ddagger increase as the concentration of free ligand increases, suggesting that the mechanism of HEH[EHP] exchange on La(AHA)₃ shifts from associative interchange to dissociative interchange mechanism.

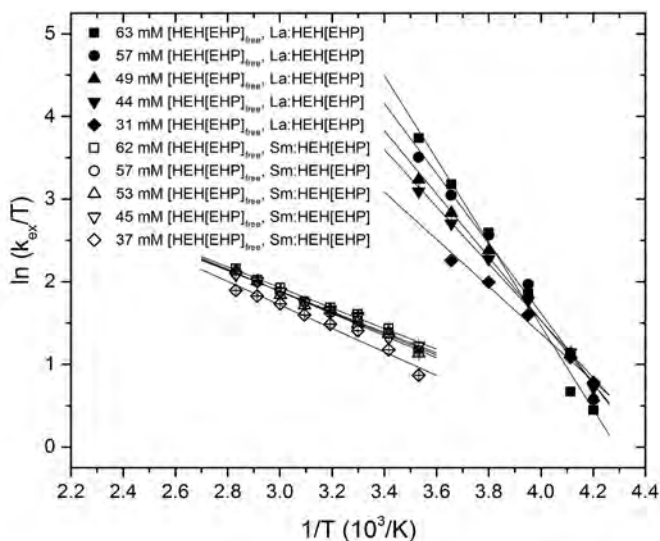


Figure 1.7. Eyring plot for the La:HEH[EHP] (filled symbols) and Sm:HEH[EHP] (open symbols) systems in 1,3-dipb with varying amounts of [HEH[EHP]]_{free}.

TABLE 1.2

Activation parameters for HEH[EHP] exchange on La(AHA)₃ complexes in 1,3-dipb

[HEH[EHP]] _{free} mmol L ⁻¹	k _{ex} @ 25°C s ⁻¹	ΔH [‡] kJ mol ⁻¹	ΔS [‡] J mol ⁻¹ K ⁻¹
63.2±0.3	3.38(±0.15)×10 ⁴	42.0±2.3	-17±9
56.9±0.5	2.31(±0.12)×10 ⁴	35.2±1.9	-43±7
48.5±0.3	1.63(±0.09)×10 ⁴	31.8±1.7	-58±6
44.5±0.2	1.28(±0.06)×10 ⁴	28.7±1.1	-70±4
31.2±0.2	7.43(±0.63)×10 ³	23.4±1.4	-91±5

An isokinetic plot was generated from the enthalpies and entropies of activation for the HEH[EHP] exchange on La³⁺ reactions (Figure 1.8A). Through a linear regression fit, these points define a line with a slope of 0.250(±0.002) that corresponds to an isokinetic temperature of 250 K (-23°C). The fact that an isokinetic relationship exists would support a single exchange mechanism operating in this system. It is possible that above this temperature data could deviate from a single mechanism system. The plot of the rate constants at the respective temperatures versus the [HEH[EHP]]_{free} (Figure 1.8,B) displays the similarities for the rate constants around -20°C. As the temperature increases, deviations of non-linear concentration dependence on the calculated rate constant are observed, particularly at room temperature (25°C).⁴ A plot of the reciprocal rate constant versus the reciprocal concentration of free HEH[EHP] gives a straight line suggestive of an interchange mechanism (Figure 1.9, equation 4).

$$k_{ex} = \frac{k_1 K [HEH[EHP]]_{free}}{1 + K [HEH[EHP]]_{free}} \quad (4)$$

⁴ Room temperature (25°C) exchange rate constants were extrapolated from collected data using the Eyring relationship.

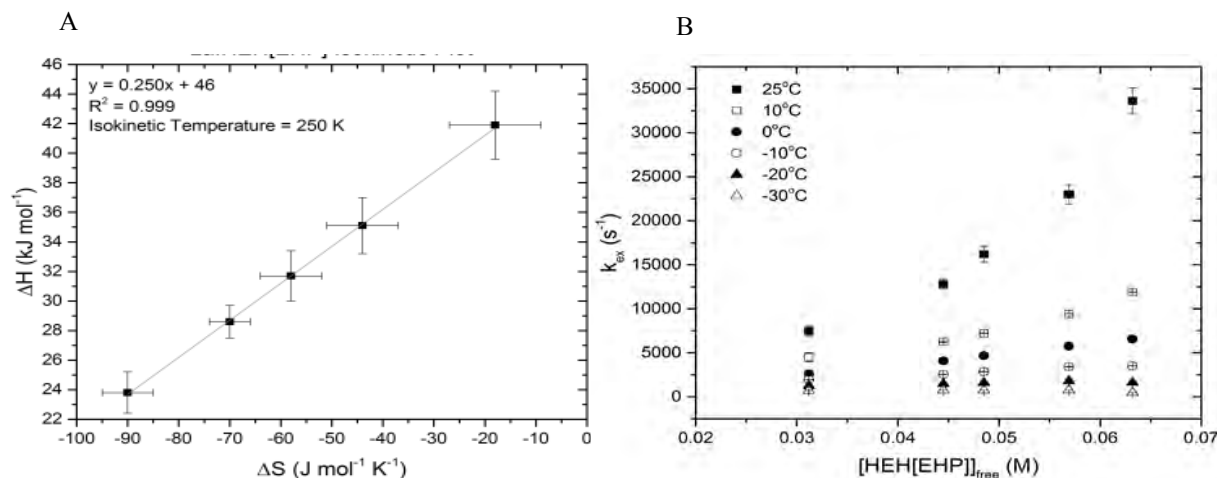


Figure 1.8. Isokinetic plot for La:HEH[EHP] (A) and exchange rate constants versus $[HEH[EHP]]_{free}$ at the different temperatures investigated.

The rate constant for the interchange exchange of HEH[EHP], k_i , can be derived from the y-intercept of the line (intercept = $1/k_i$) and the formation constant of the outer-sphere complex, K , can be derived from the slope of the line (slope = $1/k_i K$).

Through the linear regression fit of the data in Figure 1.9, a negative value for k_i is determined; however, a rate constant cannot be negative. Based on this fact, it is suggested that the mechanism for HEH[EHP] exchange on La(AHA)₃ proceeds via two different mechanisms depending on the $[HEH[EHP]]_{free}$. At lower concentrations of free ligand (less than about 30-35 mmol L⁻¹), the reaction proceeds independently of ligand concentration through a dissociative mechanism, with a k_D around $7.4(\pm 0.6) \times 10^3$ s⁻¹ (or a value close to the one calculated for 31 mmol L⁻¹ free ligand, Table 1.2). With less ligand in the bulk, there might not be enough to form the outer sphere complex necessary for the reaction to proceed with more the character of an interchange mechanism.

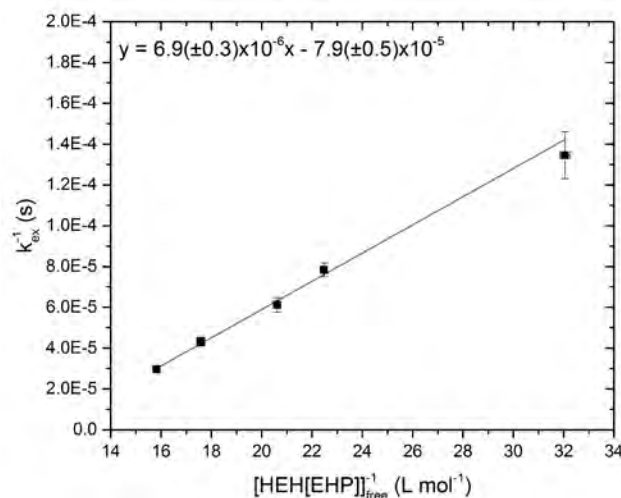


Figure 1.9. A plot of the reciprocal rate constant versus the reciprocal $[HEH[EHP]]_{free}$.

As the concentration of free ligand increases past the point mentioned above a new mechanism becomes the dominant mechanism. At higher concentrations of free HEH[EHP], the exchange reaction proceeds via an interchange mechanism, with some dissociative-like character, based on the activation parameters presented in Table I. The rate constant for the interchange mechanism, k_i , cannot be distinguished from the formation constant, K , due to the negative intercept of the line, however, the product of the two is $k_i K = 1.45(\pm 0.06) \times 10^5$ s⁻¹. There is a wide range in the sets of activation parameters, ΔH^\ddagger between 24 - 42 kJ mol⁻¹ and ΔS^\ddagger between -91

and $-17 \text{ J mol}^{-1} \text{ K}^{-1}$; however, in general, these could support the postulation of an interchange mechanism.

IV.B. Suggested mechanism of HEH[EHP] exchange on Sm(AHA)_3 complexes in 1,3-dipb

Moving across the lanthanide series, different results are observed for the HEH[EHP] exchange on Sm(AHA)_3 complexes in 1,3-dipb. Sm^{3+} has low magnetic susceptibility that allows these experiments to be performed without significant paramagnetic line broadening. Varying the concentration of free ligand from 38 mmol L^{-1} to 63 mmol L^{-1} HEH[EHP] has little effect on the exchange rate constants and activation parameters (Table II) derived from the Eyring plots (Figure 1.8, open symbols). The exchange rate constants are about ten times slower than those observed for exchange on La(AHA)_3 . The slower exchange rates represent stronger complex interactions between Sm^{3+} and HEH[EHP] when compared to the more labile La^{3+} and HEH[EHP] complexes.

The activation parameters, lower ΔH^\ddagger close to 10 kJ mol^{-1} and very negative ΔS^\ddagger around $-150 \text{ J mol}^{-1} \text{ K}^{-1}$, are suggestive of HEH[EHP] exchange on Sm^{3+} proceeding via an associative mechanism. In contrast to this, the exchange rate constants show no dependence on the free HEH[EHP] concentrations which suggests the exchange proceeds via a dissociative mechanism, represented by $k_{\text{ex}} = k_{\text{D}}$ with $k_{\text{D}} = 1210 \pm 40 \text{ s}^{-1}$.⁵

TABLE II

Activation parameters for HEH[EHP] exchange on Sm(AHA)_3 complexes in 1,3-dipb

$[\text{HEH[EHP]}]_{\text{free}}$ mmol L^{-1}	k_{ex} @ 25°C s^{-1}	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{ K}^{-1}$
63.4 \pm 0.1	1.32(\pm 0.08) $\times 10^3$	10.3 \pm 0.5	-150 \pm 2
57.9 \pm 0.2	1.24(\pm 0.04) $\times 10^3$	10.7 \pm 0.2	-150 \pm 1
54.5 \pm 0.3	1.22(\pm 0.08) $\times 10^3$	11.1 \pm 0.5	-149 \pm 2
45.2 \pm 0.2	1.26(\pm 0.08) $\times 10^3$	10.4 \pm 0.5	-151 \pm 2
38.1 \pm 0.2	1.01(\pm 0.12) $\times 10^3$	11.8 \pm 0.9	-148 \pm 3

The dissociative mechanism for HEH[EHP] exchange on Sm^{3+} is a logical mechanism for exchange. The Sm^{3+} ion is smaller than the La^{3+} ion; therefore, there is less room for the bulky incoming ligand to associate and create the higher coordination number intermediate. However, the activation parameters do not agree with a dissociative mechanism ($\Delta H^\ddagger = 10.9 \pm 0.2$ and $\Delta S^\ddagger = 150 \pm 1$)⁶ and suggest more associative character. The very negative entropy could arise from a solvent effect, where the aromatic 1,3-dipb causes an ordering around the cation. A possible explanation for the lower enthalpy of activation could arise from a monomer of HEH[EHP] from a coordinated dimer exchanging with a monomer of HEH[EHP] from a dimer in the bulk, represented in equation 6.



For this mechanism to be plausible there should be an ordering of the bulk HEH[EHP] dimers in the second coordination sphere of the Sm(AHA)_3 complex without the formation of a complex.

⁵ The k_{D} value represents the average of the k_{ex} values presented in Table II.

⁶ Activation parameters are an average of those presented in Table II.

This allows for the easy exchange of the monomer through formation of new hydrogen bonding interactions between the leaving monomer and bulk half-dimer as well as the entering monomer and the coordinated half-dimer. The rate limiting step would be the dissociation of the leaving monomer with the closing of the chelate ring of the “new coordinated” dimer happening quickly. This is one plausible explanation based on the data collected. However, cation exchanging extractants are a system that could have multiple postulated mechanisms, due to the formation of dimers in the organic phase.

IV.C. Investigations into HEH[EHP] exchange on La^{3+} or Sm^{3+} in different diluents

Valuable information concerning HEH[EHP] complex formation in the organic phase can be gained through changing the nature of the diluent. Investigations have begun into HEH[EHP] exchange in an aliphatic diluent, *n*-octane, or in a more polar environment, through the addition of 1-octanol.

HEH[EHP] exchange on La^{3+} or Sm^{3+} was investigated in *n*-octane; the Eyring plots generated from the CBS analysis for these systems is presented in Figure 1.10. The rate constant data and activation parameters presented in Table 1.3 suggest HEH[EHP] exchange on La^{3+} or Sm^{3+} in *n*-octane have similar exchange rate constants as in 1,3-dipb, suggesting the exchange rate is similar in both diluents. Differences are observed in the activation parameters. For the La^{3+} system, the enthalpy and entropy of activation are both lower in octane than a system with

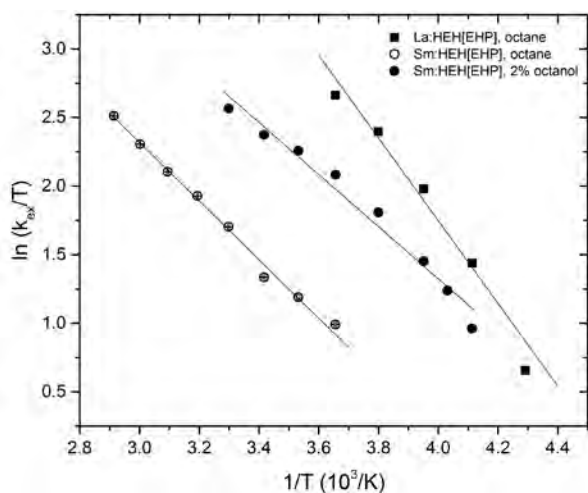


Figure 1.10. Eyring plot for the La:HEH[EHP] and Sm:HEH[EHP] systems in octane and Sm:HEH[EHP] in 2% octanol, octane.

similar free concentration of ligand in 1,3-dipb. The opposite is seen in the Sm^{3+} system, where the enthalpy and entropy of activation are higher in octane than 1,3-dipb. Based on these initial data for *n*-octane, in the La^{3+} :HEH[EHP] system *n*-octane gives the exchange more associative-like character and Sm^{3+} :HEH[EHP] in *n*-octane is has slightly more dissociative-like character. These results support the solvent having an effect on the HEH[EHP] ligand exchange mechanism. Further data should be collected by varying the concentration of free ligand and altering the diluent (to isooctane and/or toluene) to gain further knowledge into how the solvent affects the exchange mechanism.

TABLE 1.3

Activation parameters for HEH[EHP] exchange on $\text{Ln}(\text{AHA})_3$ complexes in various diluents

Diluent	k_{ex} @ 25°C s^{-1}	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{K}^{-1}$
La:HEH[EHP] system			
1,3-dipb	$1.63(\pm 0.09) \times 10^4$	31.8 ± 1.7	-58 ± 6
<i>n</i> -octane	$1.20(\pm 0.12) \times 10^4$	25.1 ± 2.4	-83 ± 9
Sm:HEH[EHP] system			
1,3-dipb	$1.24(\pm 0.04) \times 10^3$	10.7 ± 0.2	-150 ± 1
<i>n</i> -octane	$1.42(\pm 0.12) \times 10^3$	17.8 ± 0.7	-125 ± 2
2% 1-octanol, <i>n</i> -octane	$3.83(\pm 0.35) \times 10^3$	15.8 ± 1.0	-123 ± 4

Octanol has been used as a phase modifier to prevent the formation of a third phase during solvent extraction. 1-octanol was added in varying amounts (0% - 10%) to the *n*-octane system and ^{31}P NMR spectra were collected at room temperature (Figure 1.11). For HEH[EHP] exchange on La^{3+} , a broad peak is observed at room temperature, with no octanol (Figure 7, top). As the concentration of 1-octanol is increased, this peak becomes sharper, qualitatively representing an increase in exchange between the bulk and coordinated HEH[EHP] from fast to very fast exchange. The room temperature spectrum for HEH[EHP] exchange on Sm^{3+} has two peaks that are not completely resolved, representing slow exchange between the two sites (Figure 1.11, bottom). As the concentration of 1-octanol is increased, these two peaks begin to coalesce, and at 10% 1-octanol a single peak is observed, representing fast exchange.

In the La^{3+} system in octane, the collection of the spectrum at the lowest temperature (-40°C) was close to the freezing point of octane ($\sim 55^\circ\text{C}$); it is likely that the increase in exchange rate wouldn't allow for the collection of spectra in the slowest exchange regions. Therefore, the Sm:HEH[EHP] system in 2% octanol, octane was chosen to begin variable temperature NMR studies. Performing CBS analysis on the spectra collected from -30°C to 30°C allowed the generation of

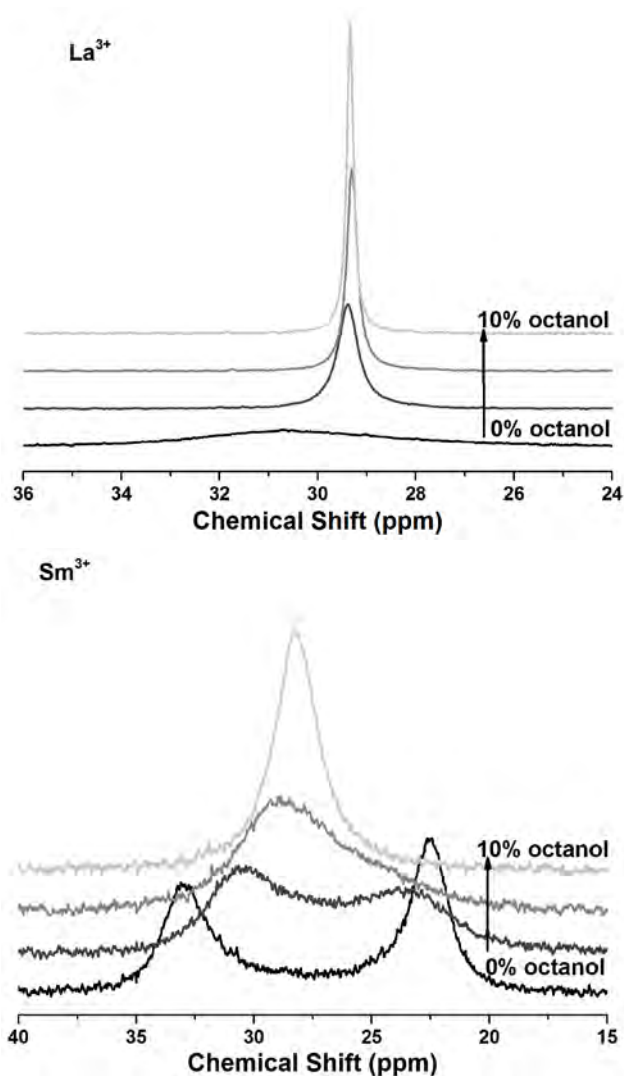


Figure 1.11. ^{31}P NMR spectra of 0.1 mol L^{-1} HEH[EHP] in varying concentrations of 1-octanol in at 22°C after equilibration with La^{3+} (top) or Sm^{3+} (bottom).

an Eyring plot (Figure 1.10) and the calculation of the exchange rate constant (at 25°C) and activation parameters (Table 1.3). The activation parameters are similar to the octane system, but the exchange rate constant is almost three times as fast in the 2% 1-octanol as compared to the octane system. For organometallic substitution reactions, it has been shown that solvents that could coordinate to an intermediate increase the reaction rate.¹² It seems possible that the 1-octanol is coordinating to the intermediate in such a way as to speed up the HEH[EHP] exchange reaction, while having little effect on the activation parameters.

V. CONCLUSIONS

HEH[EHP] exchange has already been reported to have slower exchange rates than HDEHP, suggesting stronger bonding interactions between the more basic extractant molecule.⁷ Investigation of the system with varying [HEH[EHP]]_{free} offer insights into the mechanism of exchange. For HEH[EHP] exchange on La³⁺, it is suggested that the reaction proceeds through two different paths. The first would be a dissociative mechanism at lower concentrations of free HEH[EHP]. As [HEH[EHP]]_{free} increases, the interchange mechanism becomes dominant, with the formation of an outer sphere complex before the HEH[EHP] molecules are exchanged. Generally, the activation parameters agree with this postulated mechanism. HEH[EHP] exchange on Sm³⁺ proceeds via a dissociative mechanism, with $k_D = 1210 \pm 50 \text{ s}^{-1}$. The activation parameters determined for this mechanism ($\Delta H^\ddagger = 10.8 \pm 0.2$ and $\Delta S^\ddagger = -150 \pm 2$) are not in agreement with a dissociative mechanism, suggesting there is something further happening, such as a solvent effect on the system, or monomers of HEH[EHP] exchanging.

Initial investigations into changing the diluent to *n*-octane suggest that it has little effect on the exchange rate; however, the altering of the activation parameters support a solvent effect on the HEH[EHP] exchange system. Switching to a more polar diluent through the addition of 1-octanol, significantly increases the exchange rate, but has little effect on the activation parameters, suggesting the generation of the more polar organic phase serves to increase the exchange rate. Further investigations into the exchange system in different diluents, through changing the [HEH[EHP]]_{free}, will offer further insight into complex formation in these systems.

Gaining knowledge of the ligand exchange mechanisms for HEH[EHP] on the Ln ions aids in the understanding of the overall extraction mechanism for advanced TALSPEAK processes – specifically, through beginning to gain an understanding into the mechanisms that govern complex formation in the organic phase of the system. Collection of exchange rate data and activation parameters help in forming a mechanism for exchange and complex formation between the La cation and the HEH[EHP] extractant molecule. Changing the nature of the diluent gives valuable information into the role, if any, that the diluent plays in the exchange mechanism, whether directly or indirectly.

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Task 2. Development of Entropy Titration Methods for ΔG° Determination in Unconventional Media:

This research focus grew out of studies conducted in an earlier project supported in part by a NERI grant and in part by the FCR&D Sigma Team for Minor Actinide Separations program at WSU. In that preliminary work, a discrepancy between the results of a calorimetry experiment and the predictions of thermodynamic data indicated the high probability of a lactate-specific medium effect in the free energies of complexation of Eu^{3+} by DTPA^{5-} . Of all possible experimental approaches to determining thermodynamic parameters describing complex formation, the only technique that offered the possibility of determining free energies of lanthanide-DTPA complex formation reactions in concentrated lactate buffer media was to employ the method known as an “entropy titration”. In this analysis, the variation in the heat of reaction is measured in calorimetry experiment in which the reaction does not go to completion with each addition of titrant. Analysis of a suite of titrations allows simultaneous determination of ΔG , ΔS and ΔH for the reaction. One requirement for the application of this method is for the reaction to demonstrate a significant exothermic or endothermic heat signature. The initial work was done at WSU by Dr. Travis Grimes, currently a staff member at INL.

The continuation of this work was initiated in a previous project by graduate student G. Johnson, who completed his thesis work with support from this program. Mr. Johnson measured the heats of reaction of all of the lanthanides (except Pm) as a necessary prelude to the entropy titration experiments. The trans-lanthanide pattern of heats is in general consistent with that in the prior literature aside from a predictable increase in ΔH , as shown below (Figure 2.1).

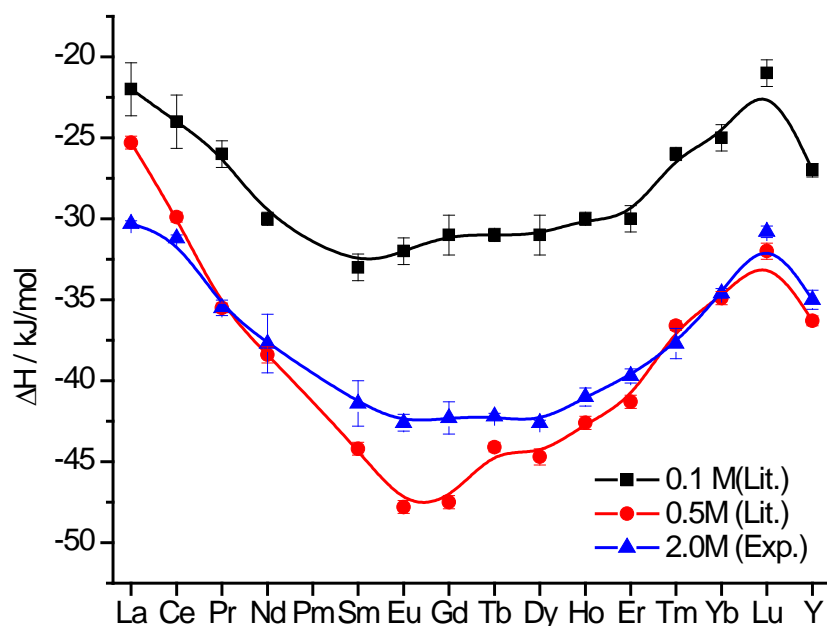


Figure 2.1. Available enthalpy data for the $\text{Ln} \cdot \text{DTPA}^{2-}$ complex from the literature at different ionic strengths (\square) 0.1 M (K^+ salt), (\circ) 0.5 M (NaClO_4), (Δ) 2.0 M plotted to show the ionic strength dependence.

Calculation of the predicted phase transfer enthalpies in conventional TALSPEAK indicated that these parameters combined with the best information from the literature on extraction enthalpies do not reproduce the observed experimental extraction heats for conventional TALSPEAK, as will be demonstrated below. This result establishes the essential need for a more direct method for determination of the heat of this reaction. In the context of fuel cycle separations development, such data impacts the accuracy of thermodynamic modeling and so is important in the prediction of process performance and for ensuring the accountability of radioactive materials.

The determination of lanthanide-DTPA complexation enthalpies at high ionic strength enabled a comparison of the observed enthalpies of the individual components of TALSPEAK with the observed net enthalpy of the process as determined by Nilsson. To do this, the individual enthalpies of each step in the series of reactions required to move a lanthanide ion from the aqueous phase to the organic phase were added to one another. This model starts with the lanthanide ion in a stable complex with DTPA in the aqueous phase. It is necessary to first decomplex the lanthanide from DTPA, then extract the lanthanide into the organic phase (releasing three protons per extracted metal ion), and finally to re-protonate DTPA^{5-} to $\text{H}_3\text{DTPA}^{2-}$. The possibility that the liberated protons might be absorbed by the lactate buffer instead of DTPA^{5-} was considered. However, DTPA^{5-} and HDTPA^{4-} are both significantly more basic than Lac^- . The formation of HLac could be expected to compete with the formation of $\text{H}_3\text{DTPA}^{2-}$, but both protonation reactions have similar enthalpy values; which reaction occurs

does not therefore significantly affect the model. The observed enthalpies for the DTPA decomplexation reaction, the HDEHP-facilitated phase-transfer reaction, and all relevant protonation and deprotonation reactions were summed to obtain the heat of extraction one would expect in an ideal TALSPEAK system. The data used to construct the model for europium are provided as an example in table 5. The ideal net reaction enthalpy was then compared to the experimentally determined enthalpy of the TALSPEAK process, showing a discrepancy of 27.7 kJ/mol for the europium extraction.

Stage	Reaction	ΔH / kJ/mol
Breaking of EuDTPA^{2-} complex (This work)	$\text{EuDTPA}^{2-} \rightleftharpoons \text{Eu}^{3+} + \text{DTPA}^{5-}$	42.6 ± 0.5
Extraction to organic layer (Zalupski et al.)	$\text{Eu}^{3+} + 3(\text{HA})_{2,\text{org}} \rightleftharpoons \text{Eu}(\text{AHA})_{3,\text{org}} + 3\text{H}^+$	-13.1 ± 1.2
Reprotonation of DTPA^{5-} (This work)	$\text{DTPA}^{5-} + \text{H}^+ \rightleftharpoons \text{HDTPA}^{4-}$	-30.3 ± 0.1
	$\text{HDTPA}^{4-} + \text{H}^+ \rightleftharpoons \text{H}_2\text{DTPA}^{3-}$	-24.6 ± 0.1
	$\text{H}_2\text{DTPA}^{3-} + \text{H}^+ \rightleftharpoons \text{H}_3\text{DTPA}^{2-}$	-9.8 ± 0.1
Calculated net extraction		-35.2 ± 1.3
Experimental net extraction (Nilsson et al.)	$\text{EuDTPA}^{2-} + 3(\text{HA})_{2,\text{org}} \rightleftharpoons \text{Eu}(\text{AHA})_{3,\text{org}} + \text{H}_3\text{DTPA}^{2-}$	-7.5

Table 5. Calculation of the enthalpy of an ideal TALSPEAK extraction of europium. The calculated enthalpy for the entire process (net extraction enthalpy) is the sum of the enthalpies of all reactions known to be involved in the process (breaking of EuDTPA^{2-} complex, extraction to organic layer, and reprotonation of DTPA^{5-}). All experimental values were obtained in NaNO_3 media at 2.0 M ionic strength and 25°C. A large discrepancy is noted between the calculated and experimental values.

As shown in figure 2.2, the energetic discrepancy observed for the extraction of europium in an ideal system vs. an experimental system remains relatively constant across the entire lanthanide series. The similarity between the experimental enthalpies of the extraction reaction and the full system has previously been taken to indicate that the extraction step is the primary contributor to the heat evolved by the TALSPEAK process and that the DTPA decomplexation step is only a minor contributor. In light of the thermodynamic data produced by this study, it seems that the breakup of the MDTPA^{2-} complex has a large effect on the overall enthalpy of a TALSPEAK extraction. This enthalpy contribution is roughly compensated for by endothermic contributions from some unknown reaction or set of reactions. These reactions are likely related to the poorly-understood behavior of the lactic acid/lactate buffer used in TALSPEAK.

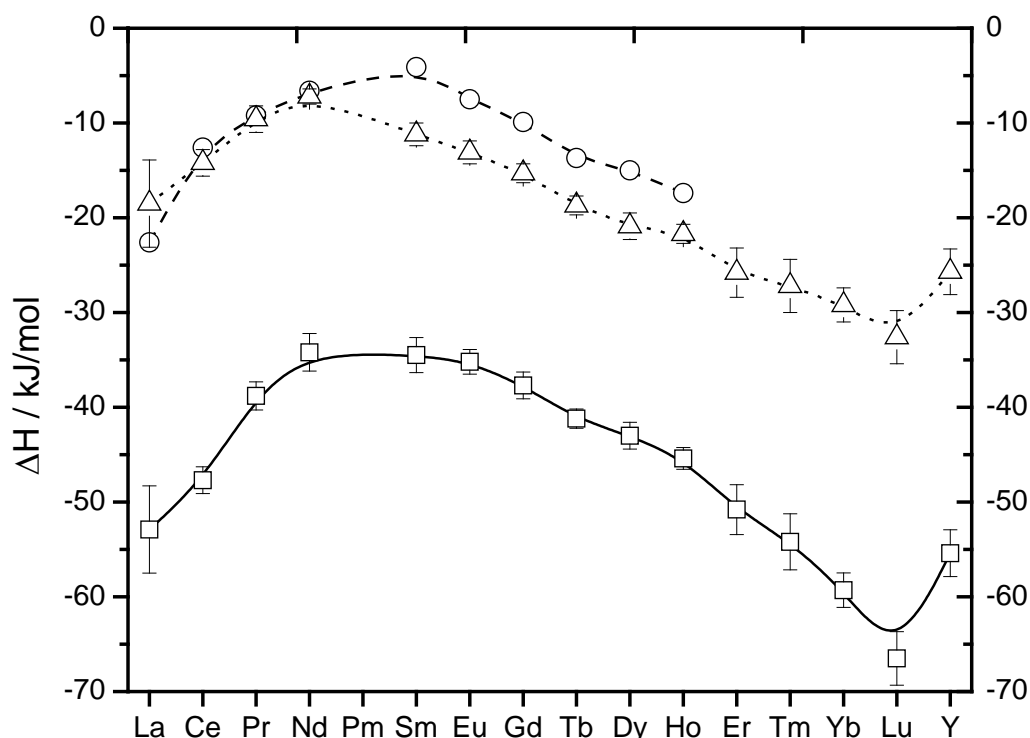


Figure 2.2. Enthalpies of: the extraction of the lanthanides by HDEHP alone (Δ); the ideal TALSPeAK system as modeled by sum of the individual enthalpies of the extraction reaction, the M-DTPA complexation reaction, and all relevant protonation steps (\square); and the entire TALSPeAK system, as experimentally determined (\circ). All values are at $I = 2.0$ M and 25°C . Lines are included to guide the eye, and do not denote any mathematical fit.

Unfortunately for this project, Mr. Johnson chose to terminate his chemistry career at the M.S. stage to pursue opportunities in environmental science with the National Oceanographic and Atmospheric Agency (NOAA). In the Spring quarter 2013 first year graduate student Jeff Berry accepted primary responsibility for this project. Mr. Berry is currently a Ph.D. candidate. His approach to continuing this project and accomplishing the required tasks are described in the following.

Development of Entropy Titration Methods for ΔG° Determination in Unconventional Media: The initial target for investigation and method development in this project is the praseodymium-lactate-DTPA system relevant to conventional TALSPeAK. As explained above, earlier work has established that in homogeneous aqueous media thermodynamic model calculations do not predict the observed Ln-DTPA complexation enthalpies seen in TALSPeAK simulant systems based on concentrated lactate buffers. This project focuses on applications of microcalorimetry to metal complexation reactions to enable the simultaneous determination of complexation enthalpy and entropy in the same experiment, following a methodology developed by Izatt and Christensen in the 1970s. The TALSPeAK system is of continued interest for these experiments,

as we have previously developed an internally-consistent set of relevant thermodynamic data that enables our analysis of the ongoing Pr-lac-DTPA entropy titration experiments. Simultaneously determining enthalpies and entropies of reactions using the method of "entropy titration calorimetry" should provide better predictive models. After experiencing some instrumental challenges, Ph.D. student Jeff Berry has recently completed several successful entropy titrations, starting with a direct determination of the thermodynamic parameters for the reaction $\text{Pr}(\text{Lac})_3 + \text{H}_3\text{DTPA}^{2-} = \text{PrDTPA}^{2-} + 3 \text{HLac}$ in 1 M lactate/2 M ionic strength media at 25°C. The 2014 addition of postdoc Lapka, who has previous experience in calorimetry (in fact with an identical instrument) and the increasing sophistication of Berry's skills advanced the pace of progress on this challenging task.

In an attempt to develop a new method of characterizing the fundamental thermodynamic parameters describing interactions in a complex medium, calorimetric entropy titrations have been undertaken. The concept of this technique is the determination of enthalpy and entropy in the same experiment, as opposed to the more conventional approach of first determining ΔG° then ΔH° in a separate experiment to enable calculation of ΔS° . This approach requires expected free energy values within a comparatively narrow range and demands attention to detail in the analysis, but offers a useful shortcut to the determination of thermodynamic parameters. Utilizing praseodymium as an initial lanthanide for study, solutions of praseodymium-lactate have been titrated with a DTPA-lactate solution. The titrations have been conducted at 2 M total ionic strength, maintained with sodium nitrate, with a praseodymium concentration of 0.005 M and a lactate concentration of 1.0 M, at a pH of ~3.6. The solution is titrated with a 0.051 M solution of DTPA, also at 1.0 M lactate, pH 3.6 and an ionic strength of 2.0 M maintained with sodium nitrate. A sample titration is seen in figure 2.3.

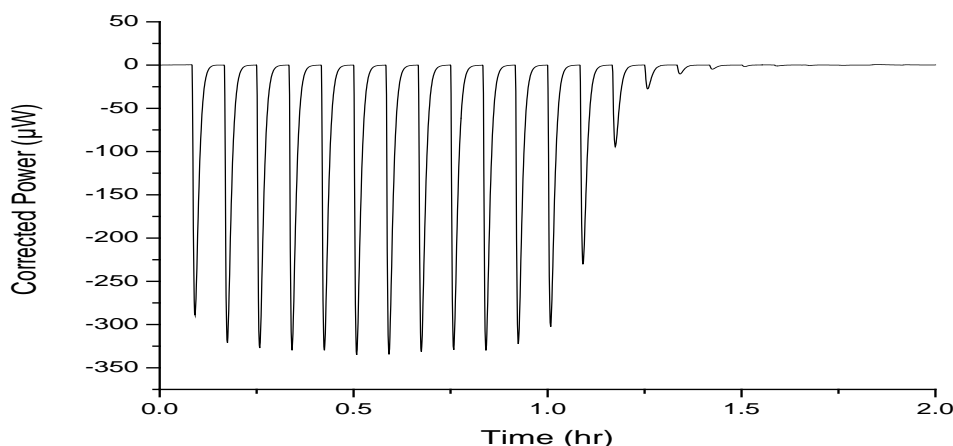


Figure 2.3. Titration of 5 mM $\text{Pr}(\text{lac})_3$ with 51 mM DTPA, 1 M total lactate, pH 3.6, ionic strength 2.0 M.

In order to reduce the signal-to-noise ratio, and to ascertain the ideal concentrations for the titrations, an experiment was carried out using higher concentrations of both praseodymium and DTPA, while maintaining the total ionic strength and the lactate concentration (figure 2.4). While the signal does increase, this increase in the concentrations of the species also changes the total ionic strength of the final solution, and consequently 5 mM was chosen for future solutions. The decreased curvature seen in the more concentrated solutions is potentially beneficial, and this suggests that a smaller volume of injection would allow better determination of the value of $\log K$.

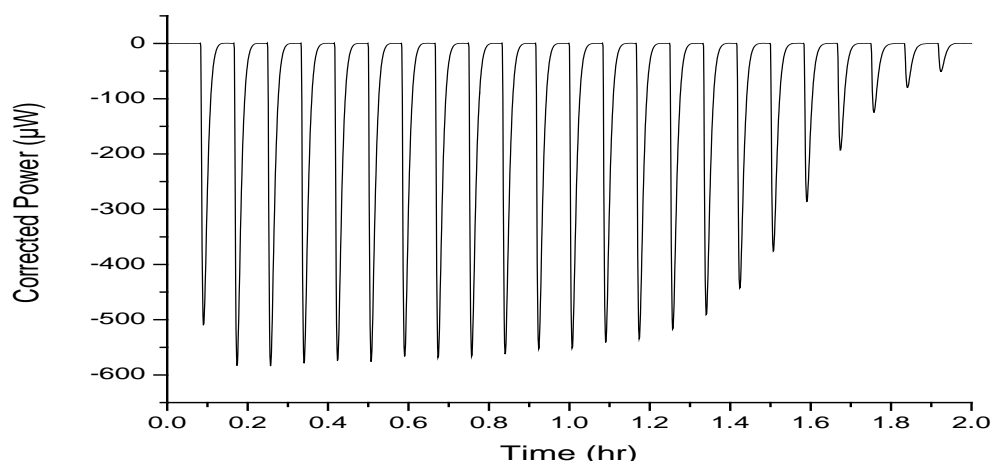


Figure 2.4 Titration of 15 mM $\text{Pr}(\text{lac})_3$ with 75 mM DTPA, 1 M total lactate pH 3.6, 2 M total ionic strength.

In addition to these titrations, to determine the enthalpy of binding for the tris-lactate solution, a titration of $\text{Pr}(\text{lac})_3$ with nitric acid was conducted (figure 2.5). If the volume of the titrant is decreased, then the curvature of the thermogram may be used to determine the binding constants of the lactate to the praseodymium. These constants are being independently measured at 2 M ionic strength via potentiometric titrimetry. This is done by making a solution of praseodymium that is 10 mM in Pr^{3+} , 150 mM in lactate, and 2 M in total ionic strength (maintained with NaNO_3), and titrating with a 1 M HNO_3 solution with 1 M NaNO_3 . These data are fit with Hyperquad 2008.

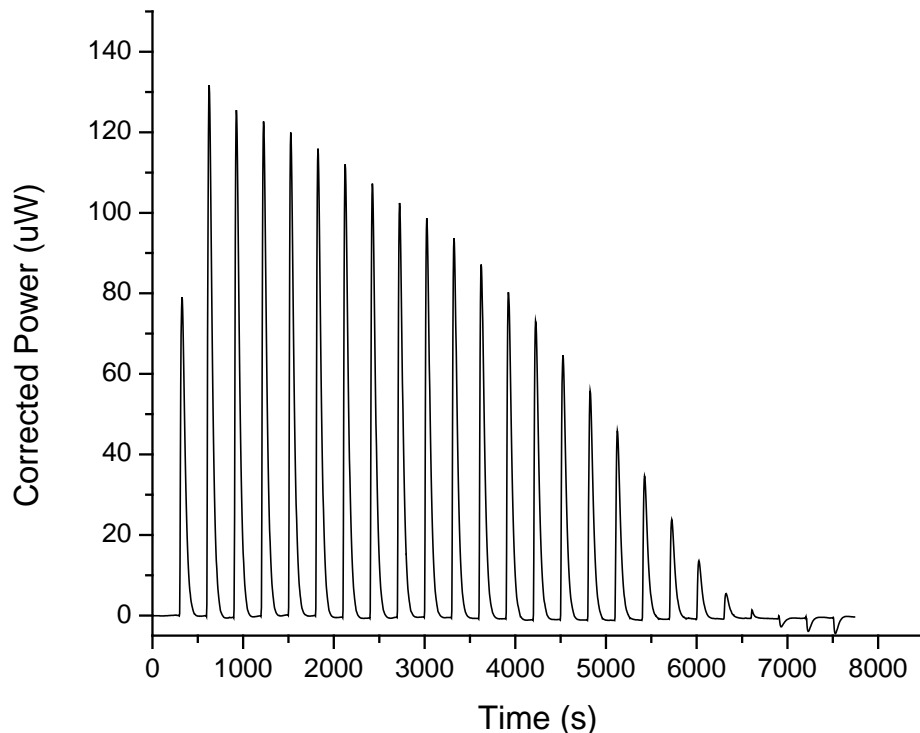
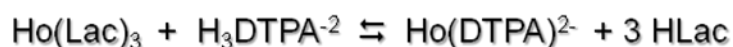
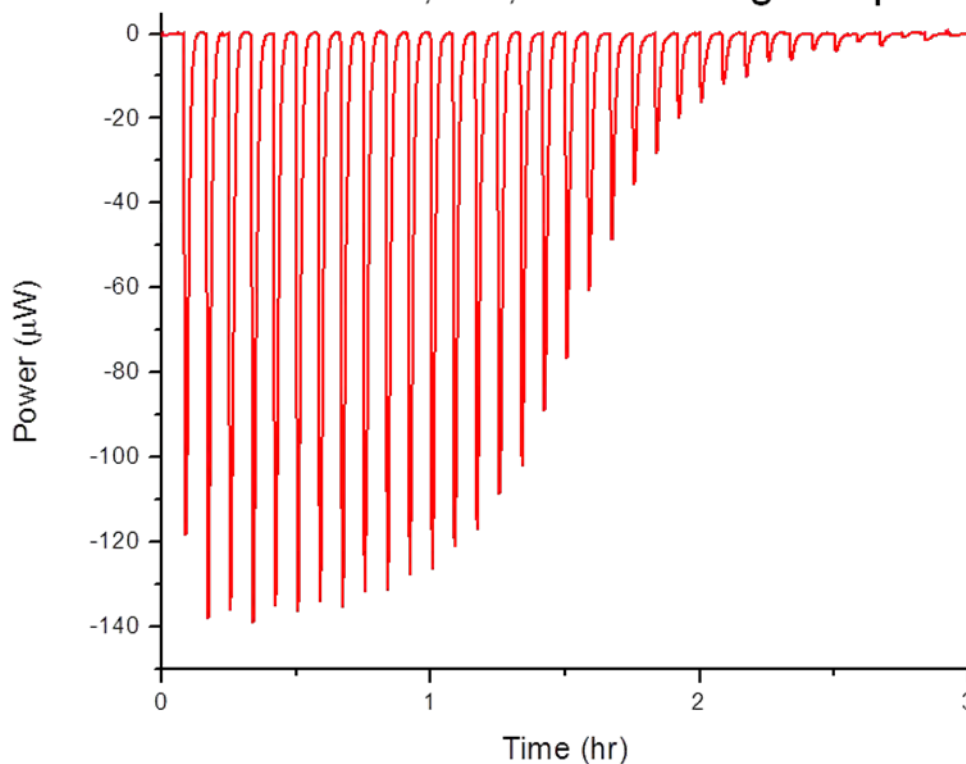


Figure 2.5 Calorimetric titration of 10 mM $\text{Pr}(\text{lac})_3$ with 0.5 M HNO_3 , 2 M ionic strength.

To accelerate progress in these studies and to improve reproducibility between runs, 500 mL of a standard solution of 1.0 M total lactate with 1.0 M NaNO₃ at a pH of 3.6 was prepared for the purposes of maintaining consistency and minimizing variability, for solutions across the lanthanide series. Solutions of 25 mL are drawn from this stock, and the lanthanide of interest is added to a final concentration of 5 mM Ln(III). A second 250 mL solution of DTPA at 51 mM, 1.0 total lactate and 0.9 M NaNO₃ at a pH of 3.6 was prepared for the titrations of the whole lanthanide series (minus Pm, plus Y). The remaining lactate-nitrate solution, as well as a separate solution of nitrate, is used to determine dilution heats of the DTPA-lactate solution. Periodic titrations of standard 18-Crown-6 ether with BaCl₂ must be conducted between trials, to ensure that the calorimeter is calibrated, and the calibration factor does not drift. Results of successful entropy titrations are reported in the table below. These results confirm a contribution of a lactate-specific activity contribution to the net interaction strength and seemingly indicate a trans lanthanide trend across the series. A sample titration of Ho(Lac)₃ by H₃DTPA²⁻ at 2 M ionic strength is shown below to demonstrate the increasing quality of the data generated using this technique. The plan going forward on this task (for the duration of Berry's Ph.D. research) is to complete similar experiments on some number of lanthanide complexes to assess the apparent pattern of stability and to correlate the results with our earlier data on the two component (lanthanide - lactate or lanthanide DTPA) systems to assess the origin of any discrepancies noted. Developing a specific molecular level explanation for this effect will ultimately prove more difficult. But the complementary nature of applying different tools (developed here) will help firm up interpretations of the features of this system. An ambitious next stage of such studies might well shift our focus toward applying these methods to biphasic titration calorimetry. The further extension to elevated temperature operations could add yet another dimension.

	La³⁺	Pr³⁺	Gd³⁺	Yb³⁺
$\Delta G_{\text{calorimeter}}$	-9.2 kJ/m	-16.7 kJ/m	-29.5 kJ/m	-24.3 kJ/M
ΔG_{model}	-17.1 kJ/m	-22.3 kJ/m	-26.9 kJ/m	-18.4 kJ/m
$\Delta G_{\text{c}} - \Delta G_{\text{m}}$	+6.9 kJ/m	+5.6 kJ/m	-2.6 kJ/m	-5.9 kJ/m

Entropy Titration $\text{Ho}(\text{Lac})_3 \rightarrow \text{Ho}(\text{DTPA})$: Determination of ΔG , ΔH , ΔS in a Single Experiment



In other work directed at describing the thermochemistry of solvent extraction systems (studies also relevant to Task 3), Dr. Lapka investigated the thermodynamics of lanthanide interactions with DTPA (and similar reagents) in concentrated malonate media using optical spectroscopic methods, confirming and extending the work begun by departed postdoctoral research associate Wahu. Malonate is of interest as an alternative to lactate/citrate in TALSPEAK/Advanced TALSPEAK separations; this system is also of interest as a follow-on candidate for entropy titration studies. A manuscript on advanced TALSPEAK separation systems based on malonate buffering has been published. Mixed-ligand complexes between HEDTA and the malonate buffer have been established in both distribution studies and spectrophotometry. A second manuscript describing the thermodynamics of Nd and Am mixed – ligand complexes is nearly ready for submission to either Dalton Transaction or Inorganic Chemistry. The malonate-buffered option for Advanced TALSPEAK features a flat pH dependence over the range of pH = 2.5-4.0. Preliminary process analysis suggests that the flat pH dependence of this extraction system arises from the presence of these mixed-ligand complexes in the aqueous phase.

The arrival of Dr. Joseph Lapka (coincident with the departure of Dr. Wahu) resulted in this portion of the project being handed off to Dr. Lapka, who has continued the analysis and interpretation of the spectrophotometric data while also working on development of an Advanced TALSPEAK separation process based on a malonate buffer.

Spectroscopic Studies of Advanced TALSPEAK with Malonate:

Separation of the trivalent actinides and lanthanides remains a challenging task in the implementation of a fully closed nuclear fuel cycle. Recently, variations of the standard Trivalent Actinide-Lanthanide Separations by Phosphorous-reagent Extraction from Aqueous Komplexes (TALSPEAK) method have been proposed, substituting bis(2-ethylhexyl)phosphoric acid (HDEHP) with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]). Several advantages in what has been deemed as Advanced TALSPEAK can be noted by using HEH[EHP] rather than HDEHP, including a flatter pH profile, more predictable thermodynamic extraction behavior, and faster extraction kinetics relative to traditional TALSPEAK.

The partitioning and separation of the trivalent lanthanide elements and americium between an aqueous phase and n-dodecane diluent using a combination of

HEH[EHP], malonic acid, and N-(hydroxyethyl)-ethylene diaminetriacetic acid (HEDTA) has shown there to be a discrepancy between experimental distribution ratios and those predicted by thermodynamic data of the known species in solutions as shown in Figure 2.6.

With malonate the extraction model does not predict any flattening out effect of the distribution dependence at higher pH as is seen experimentally, but rather beginning to

sharply increase again after an initial leveling off around $\text{pH} = 2$. To explain this behavior, spectroscopic investigations were completed to establish the presence of a ternary metal complex with HEDTA and malonate. No accepted literature values for americium malonate stability constants exist; therefore spectrophotometric titrations of americium with malonate alone were performed. The resulting spectra are shown in Figure 2.7. Deconvolution of the spectra shows a good fit when a total of five absorbing species are included in the model: Am^{3+} , AmMal^+ , AmMal_2^- , AmMal_3^{3-} , and AmMal_2H . The stability constants for these species (Table 2.1) are consistent in magnitude with those seen in the literature for the lanthanides, particularly neodymium, which should have the most similar affinity for hard oxygen donors. The titration of an americium-malonate solution by HEDTA is shown in Figure 2.8. A new species is seen which does not correspond to those obtained for Am-malonate or Am-HEDTA species. The known spectra previously found were then used to deconvolute the spectra in order to determine the strength of the ternary complex. The obtained stability constant for the Am-HEDTA-

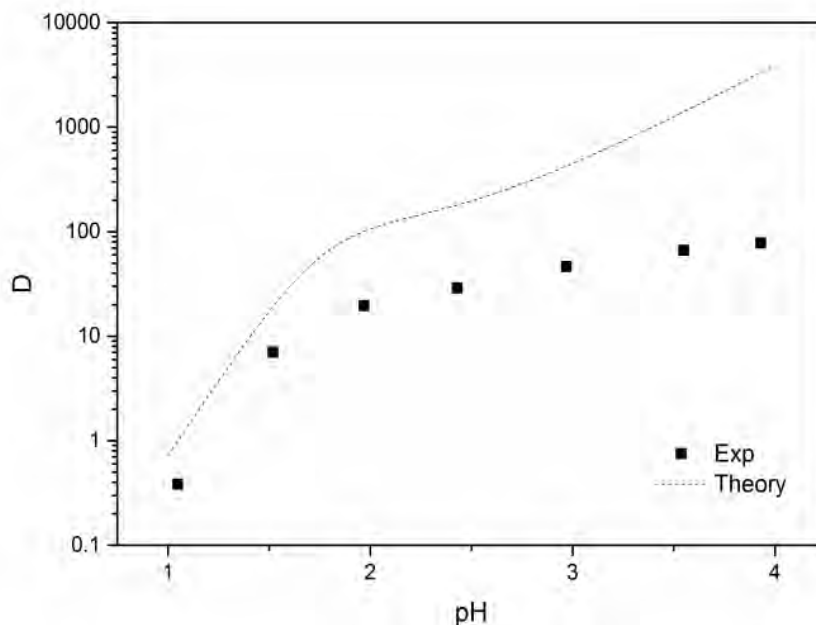
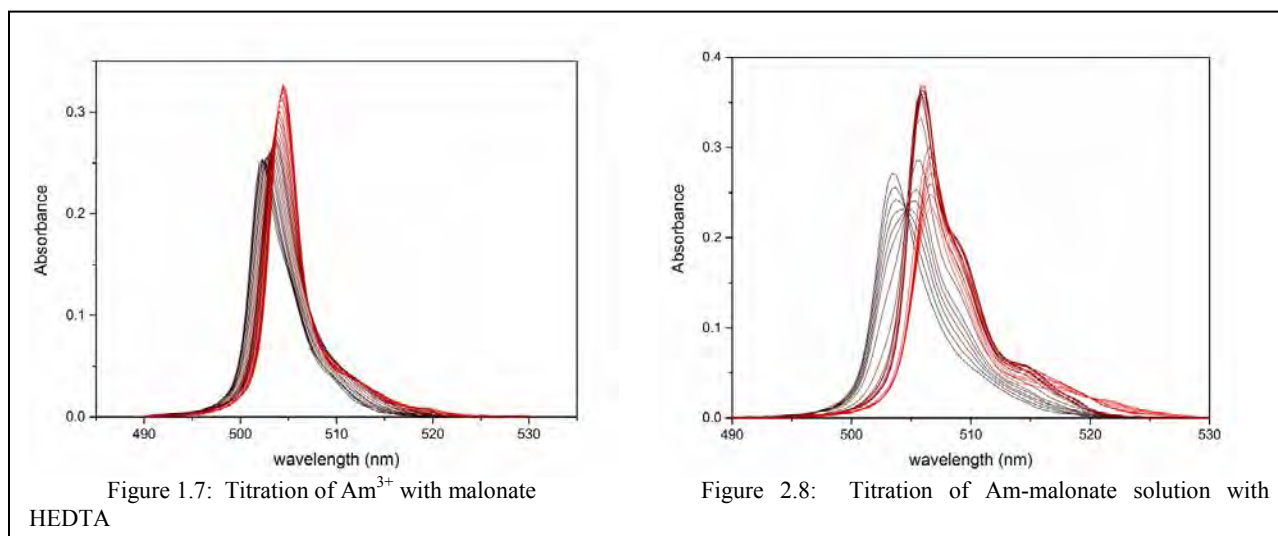


Figure 2.6: Theoretical and experimental extraction of europium by HEH(EHP) with 0.5 M malonate and 0.02 M HEDTA



malonate ternary complex is $\log \beta_{111} = 17.76 \pm 0.01$. This value is in good agreement with that obtained from solvent extraction modeling of $\log \beta_{111} = 17.90 \pm 0.04$.

Similar titrations were also performed using fluorescence with europium (Figure 2.9). Like that with americium, a new complex is seen when titration HEDTA in a solution containing europium and malonate. This new species is consistent with ternary complex formation, with a stability constant of $\log \beta_{111} = 17.31 \pm 0.06$ in excellent agreement with the value from solvent extraction of $\log \beta_{111} = 17.36 \pm 0.06$. Time-resolved fluorescence studies (Figure 2.10) have revealed that this complex displaces seven water molecules around the europium center, consistent with the coordination of pentadentate HEDTA and bidentate malonate.

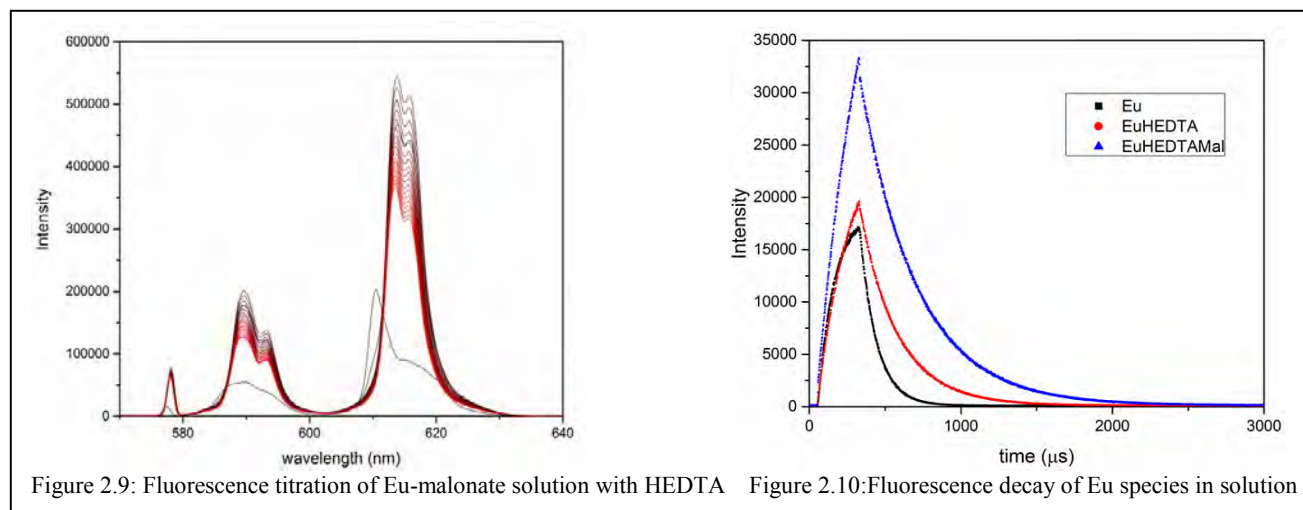


Table 2.1: Stability constants of metal complexes with malonate and HEDTA determined by spectroscopy and solvent extraction in current work		
Species	Log β	
	Extraction	Spectroscopy
Eu(HEDTA)	15.08 \pm 0.07	15.09 \pm 0.04
Eu(HEDTA)(Mal) ²⁻	17.36 \pm 0.06	17.31 \pm 0.06
AmMal ⁺		3.54 \pm 0.01
Am(Mal) ₂ ⁻		5.76 \pm 0.02
Am(Mal) ₃ ³⁻		6.66 \pm 0.03
Am(Mal) ₂ H		8.86 \pm 0.02
Am(HEDTA)	15.60 \pm 0.05	15.53 \pm 0.02
Am(HEDTA)(Mal) ²⁻	17.90 \pm 0.04	17.76 \pm 0.01

Task 3. Fundamental Interactions in mixed extractant systems/optical methods of analysis.

In this task, the initial focus was on applying optical methods and on the measurement of physical properties (e.g., surface/interfacial tension) to the development of a more detailed understanding of the interactions that characterize the properties of mixed-extractant solutions. Work complementary to our Sigma Team for Minor Actinide Separations studies of mixed extractant systems has aided in the development of methods and techniques for this subtask. Our new fluorimeter and long pathlength (100, 500 cm) capillary optical cells (acquired on NEUP infrastructure funding) enabled the application of fluorescence and absorption spectroscopy as a characterization tool. A key focus area for the development of optical methods of analysis has been characterization of malonate as a potential buffer for TALSEPAK – like separations. Using a malonate buffer enables studies at pH 2.5, at which point rates of Ln-DTPA complex formation and dissociation reactions are more rapid than is seen at pH 3.5/1 M lactate buffer. A first draft manuscript is complete and undergoing adjustments at present. Second year graduate student Harry Taylor conducted a series of experiments focusing on measuring the physical properties (viscosity, interfacial tension, density, etc.) of extractant solutions. For reasons of health, Taylor has left the program with a terminal MS degree.

In this task, the focus was on applying optical methods and the measurement of physical properties (e.g., surface/interfacial tension, organic phase water content) to the development of a more detailed understanding of the interactions that characterize the properties of mixed-extractant solutions. Much of this work ultimately targets performance predictions in mixed

extractant systems as seen in the ALSEP/TRUSPEAK/SANEX/GANEX processes being developed-demonstrated in the U.S. and abroad. Dr. C. Marie is an important resource in this portion of the project (as well as in Task1). The recent addition of a new spectrofluorimeter (acquired on NEUP infrastructure funding) has also enabled the application of fluorescence spectroscopy as a characterization tool, as was noted above. The application of f-element optical spectroscopy is not a new feature of our work; being able to do fluorescence experiments in-house is a new capability. To complement the optical spectroscopy and in anticipation of the start of another NEUP project, we have also invested some effort in the correlation of interfacial tension, measurement of water content and cation extraction in TALSPEAK-relevant systems.

During the Summer and Fall quarters of 2013 (and for several years prior to that time), the Ph.D. research of (then graduate student, now Dr.) D. Brigham focused on the application of stopped-flow spectrophotometry on the elucidation of the aqueous phase kinetics of lanthanide DTPA, EDTA and HEDTA complexation in 1 M lactate buffer media. The objective of that research was to increase understanding of lactate activity as a phase transfer catalyst in conventional TALSPEAK. A correlation of the rate of lanthanide release from LnDTPA^{2-} with the net ligand number of lanthanide lactate complexes was established. As several undesirable factors of conventional TALSPEAK arise from the need for macroscopic concentrations of lactate, alternate buffers are of interest. One possible replacement is malonic acid. To build on the previous kinetic results, we have continued to investigate lanthanide-DTPA exchange kinetics using malonate buffers. This option is connected with our interest in developing the alternative Advanced TALSPEAK process, based on HEH[EHP].

In the earlier work, correlations of rate data with thermodynamic equilibrium calculations lead ultimately to the conclusion that the primary reactants in the observed reaction are $\text{Ln}(\text{Lac})_n^{3-n}$ species interacting with either $\text{H}_3\text{DTPA}^{2-}$ or $\text{H}_2\text{DTPA}^{3-}$. In 0.3 M lactate buffer (pH 3.6), Gd^{3+} complex formation reactions are fastest for both ligand systems and Lu^{3+} is the slowest. This result appears to be most closely correlated with the equilibrium lactate-lanthanide complex stoichiometry, which is 2.46 at Gd^{3+} , 2.94 for Lu^{3+} . This result is taken as an indication of reaction inhibition by the formally neutral $\text{Ln}(\text{Lac})_3$ complex.

This research was continued with a detailed examination of the complexation kinetics of these same lanthanide ions with DTPA, EDTA and HEDTA in 1 M lactate buffer. In this investigation, it was discovered that the reaction describing the complex formation reaction of LnDTPA^{2-} occurs under TALSPEAK conditions via the formation of an unidentified $(\text{Lac})\text{Ln}(\text{DTPA})^x$ transient complex. At higher lactate concentrations the Ln-DTPA complex formation reaction slows. The activation entropy for this reaction is strongly positive, which is interpreted to require the dissociation of a lactate from a higher order $\text{Ln}(\text{Lac})_n$ species. This observation leads to the postulation of a chemical kinetics mechanism to describe Ln extraction in TALSPEAK systems as follows (considering only secondarily the influence of inter-phase transport reactions):





In this hypothetical reaction sequence, the first rate limiting process (reaction 1) is the release of the lanthanide cation from the thermodynamically stable $\text{Ln}(\text{DTPA})^{2-}$; this reaction is typically accompanied by rapid recombination reaction (reaction 2) and diffusion-controlled protonation of DTPA^{5-} (reaction 3). Such reactions have been reported in the prior literature as being subject to catalysis by H^+ and acetate buffer; the TALSPEAK-relevant work does not clearly establish H^+ involvement, though lactate ion is certainly important. Reaction 3 is not rate-process relevant since these reactions occur rapidly and spontaneously at constant pH. The high concentrations of lactate anion in TALSPEAK drives the rapid formation of 1:1, 1:2, and 1:3 complexes (as dictated by equilibrium thermodynamics – the average ligand number varies across the series in a non-linear fashion).

The tris-lactate complex presents a moderately hydrophobic outer shell (assuming that each lactate is bidentate, the residual hydration is 2-3 water molecules) thus it can more readily diffuse toward the less polar interface double layer (reaction 7). In the interface, the de-dimerized HDEHP monomer exchanges its H^+ to a lactate ion (reaction 8) and “drags” the $\text{Ln}(\text{Lac})_2(\text{DEHP})$ deeper into the organic phase where the more abundant and more hydrophobic $(\text{HDEHP})_2$ displaces the remaining lactate molecules forming the very stable and highly hydrophobic pseudo-octahedral $\text{Ln}(\text{DEHP} \cdot \text{HDEHP})_3$ complex (reaction 9). The ESI-MS, NMR, optical spectroscopy and SANS results indicate that more complex mixed ligand complexes become more important as the metal ion concentration increases to $[\text{Ln}]:[\text{HDEHP}]$ ratios less than 1:6 (HDEHP monomer equivalents) at which point apparently polynuclear, mixed-ligand complexes become more important. In this analysis, the increased hydrophobicity of $\text{Ln}(\text{Lac})_3$ and the lability (rapid ligand exchange) of these complexes would appear to represent a good combination for more rapid phase transfer kinetics.

Starting with his arrival in March 2013, postdoctoral associate Dr. G. Ferru investigated the kinetics of lanthanide complexation by DTPA and EDTA in moderately concentrated malonate buffer solutions. The potential role of malonate in TALSPEAK-like separations has been noted above. These kinetic studies complement the work briefly mentioned in Task 2 on the thermodynamics of this system. The stopped-flow technique as applied in this system relies on the ligand Arsenazo III as an optical indicator of the changing concentration of free lanthanide ion as the reaction progresses. We have found that at 0.4 M malonate and pH 2.5 the predominant reaction mechanism for most of the lanthanides progresses through the agency of a

mixed –ligand malonate-Ln-DTPA species, as indicated by the dependence of the complex formation rate on [DTPA]. This saturation kinetics mechanism was also seen in the lactate system at elevated lactate concentrations and the highest [DTPA]. These kinetic data allow estimation of an equilibrium constant for the ternary (precursor) complex and a rate constant for its dissociation. A correlation of the latest results is shown below. These data have been correlated with the earlier lactate data; these rates appear to be comparable to the lactate data, though the trans-lanthanide pattern of changing rates is different peaking at Eu rather than Gd. This investigation continues and we expect more mechanistic details to emerge. A first draft manuscript of an open literature publication from these kinetic studies is nearly ready for submission. It is likely that additional mechanistic details will be developed as this manuscript is adjusted (there are minor interpretative details that we have not yet resolved, but must prior to publication). Features of the work will be discussed in the following pages.

Kinetics of the complexation of lanthanides by DTPA in malonate media

G. Ferru^a and K. L. Nash^{a*}

Introduction

Fission of uranium in light water reactors leads to the production of lanthanides and actinides in significant amount in used nuclear fuel. While actinides could be transmuted in future generation reactors, lanthanides are considered as waste byproducts^{1,2}. To enable an efficient transmutation of transplutonium actinides, lanthanides and actinides must be mutually separated. However, their similar chemical properties (hard acid nature, overlapping ionic radii and the dominance of the trivalent oxidation state) make the separation of those elements a significant challenge²⁻⁴. Fortunately, the slightly greater covalency in the bonding interactions of actinides relative to lanthanides can be exploited to enable a chemical separation using nitrogen or sulfur donor ligands²⁻⁵.

The TALSPEAK process (Trivalent Actinide Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes) is a solvent extraction-based method for accomplishing this separation in which a liquid cation exchange reagent, for example HDEHP (di-(2-ethylhexyl) phosphoric acid) in an aliphatic or aromatic solvent (e.g., 1,4-diisopropyl benzene) is contacted with an aqueous phase containing an actinide-selective polyaminocarboxylate ligand, such as DTPA (DiethyleneTriamine-N,N,N',N'',N'''-Pentaacetic Acid) (Fig. 1). In TALSPEAK, lanthanide ions report to the organic phase while actinides remain in the aqueous phase. In this system, DTPA is called a holdback reagent⁶⁻¹². Usually, aqueous solutions in TALSPEAK process are buffered at pH 2.5 to 3.5 by lactic acid solutions, DTPA concentration could vary from 0.05 M to 0.1 M^{12,13}.

Because the phase transfer kinetics in TALSPEAK systems tends to be unacceptably slow, a high concentration of the lactic acid buffer (0.5 to 2.0 M) is generally required¹⁵. Moderating the concentration of lactic acid has shown to improve phase kinetic transfer¹⁶. It is generally considered that the slow phase transfer kinetics result from slow release of lanthanide ions from the DTPA complexes in the interface and that lactate enhances the rate of release via the formation of transient ternary Ln-DTPA-Lactate complexes^{12,17}. In an earlier study a correlation has been developed between the rate of formation of

lanthanide-DTPA complexes and the number of lactate ions associated with lanthanide ions at equilibrium.¹³

Because lactic acid is also known to increase the complexity of TALSPEAK separations through its tendency to partition into the organic phase,^{8,14} replacing lactic acid by another buffer appears to offer a possible remedy in the separation science. Malonic acid (Fig. 1) can be considered as a potential alternative to lactic acid in TALSPEAK by virtue of its somewhat more acidic pK_{a1} value and added buffering capacity arising from the second carboxylate group. Despite the presence of a second anionic binding site, the comparative strength of lanthanide lactate and malonate complexes is surprisingly similar in the pH range of interest. However, it is likely that substitution of a concentrated malonate buffer for lactate will have an influence on lanthanide-DTPA complexation kinetics. Solvent extraction studies in progress establish that 0.5-1.5 M Na/H malonate buffer will support a TALSPEAK separation system.

Preliminary kinetic studies demonstrated that the lanthanides-DTPA complexation reaction (pH 2.5-3.5) in absence of a buffer in solution is too fast to be measured by stopped-flow spectrophotometry. However, reaction rates become accessible at a stopped-flow time scale when solutions are buffered by moderate concentrations of carboxylic acids, indicating their participation in the Ln-DTPA complexes formation mechanism^{13,15}. Nash et al.¹³ have demonstrated that La-DTPA complex dissociation is inversely proportional to the lactate concentration. Complex formation was typically found to be directly dependent on $[H^+]$ concentration in lactate media¹³, which is opposite that typically observed in the complexation of lanthanides by polyaminocarboxylate ligands in acetate buffer solutions¹⁸⁻²⁰.

The following discusses the results of kinetic studies that focus on understanding the role played by the malonic acid in the formation of Ln-DTPA complexes. The equilibrium perturbation by ligand displacement method has been an effectively employed by several authors in studies of lanthanide and actinide complexation kinetics^{13,21-25}. As lanthanides form optically transparent complexes with DTPA or malonic acid in the concentration range of interest, it has been necessary to use a strongly colored auxiliary reagent. Several studies of lanthanides and actinides complexation kinetics have used a colored reagents like Arsenazo III (2,2'-(1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo)bis(benzenearsonic acid) or AAIII, see Fig. 3.1)^{13,26-27}. Complexation rate between lanthanides and AAIII are at or near the diffusion-controlled limit as shown by previous studies²¹⁻²⁷. The ability of AAIII to function as a metal complex indicator at low pH (2-3) makes AAIII a suitable indicator for kinetic studies of this type.

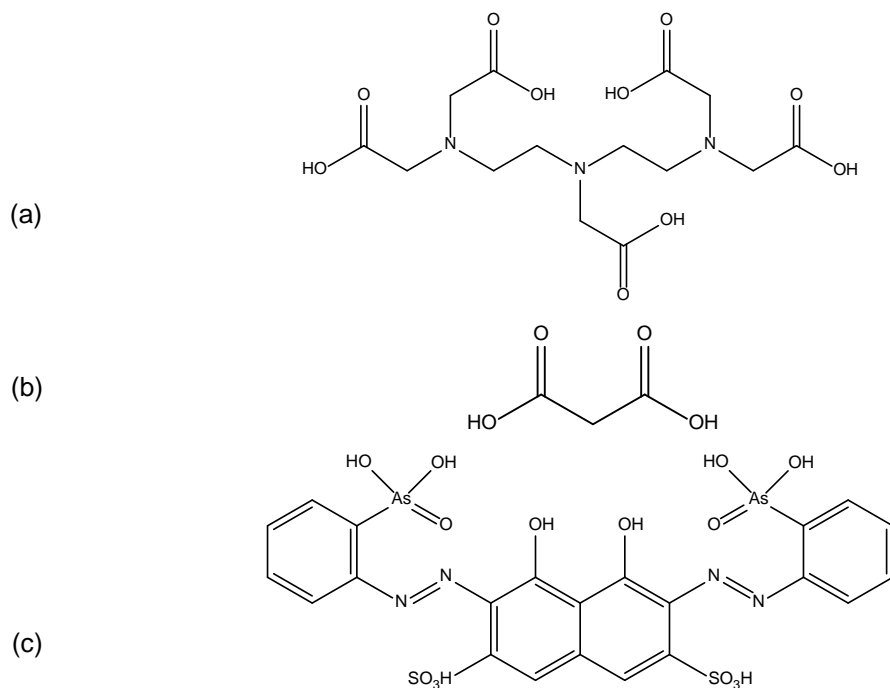


Fig. 3.2 – Structures of (a) DTPA, (b) malonic acid and (c) Arsenazo III

Apparent reaction rates of lanthanides complexation by DTPA in malonate media (0.2 to 0.4 M) are reported in this study. The influence of several parameters, including the pH, the ionic strength, the temperature and the concentrations of the different constituents of the solutions have been investigated and discussed to obtain a better understanding of lanthanide-DTPA complexation mechanism in concentrated buffer media related to TALSPEAK-like systems.

Results

Lanthanides series

Observed rate constants k_{obs} have been measured for the lanthanides series (except La^{3+} and Pm^{3+}) at pH 2.5, $I = 1 \text{ M}$, $[\text{Mal}]_{\text{tot}} = 0.4 \text{ M}$. Plots of k_{obs} versus $[\text{DTPA}]$ exhibit two distinct patterns (Fig. 3.2): for the light lanthanides (Ce^{3+} and Pr^{3+}), plots of k_{obs} versus $[\text{DTPA}]$ exhibit a straight line with a positive intercept, while for heavier lanthanides (Eu^{3+} through Lu^{3+}) a saturation effect is observed at high DTPA concentration ($> 5 \text{ mM}$). Nd^{3+} and Sm^{3+} show an intermediate behavior, for which a saturation effect is observed only for the highest concentrations of DTPA ($> 8 \text{ mM}$) and with a finite positive intercept. The observation of a saturation effect could be attributed to the formation of a precursor complex which governs the speed of the reaction. Consequently, the k_{obs} vs. $[\text{DTPA}]$ data were fit using equation (1), using three parameters, the second order rate constant or complex formation constant k_f , the first order rate constant or complex dissociation constant k_d , and the pre-equilibrium constant K_{pre-eq} .

In each system, at least two parameters were required to correlate k_{obs} with $[\text{DTPA}]$. This relation of the observed rate constant is a combination of the equation giving the observed rate constant as a linear function of the ligand concentration, with the formation and

dissociation rate constants as the slope and the intercept, respectively, under pseudo first order conditions^{13,15,32} and the equation of the observed rate constant when the pre-equilibrium assumption is applied²⁸⁻³². If no precursor species is formed, K_{pre-eq} is equal to 0 and the observed rate constant becomes a linear function of [DTPA]. On the other hand, when an intermediate species is formed, the reaction is dependent of the formation of the precursor complex which is taken into account by the pre-equilibrium constant; under these conditions, the complex dissociation reaction becomes unimportant and $k_d = 0$. The combination of those two relations of k_{obs} allows to fit the data for the whole lanthanides series with a single expression relating k_{obs} to [DTPA].

$$k_{obs} = k_d + \frac{k_f[DTPA]}{1 + K_{pre-eq}[DTPA]} \quad (1)$$

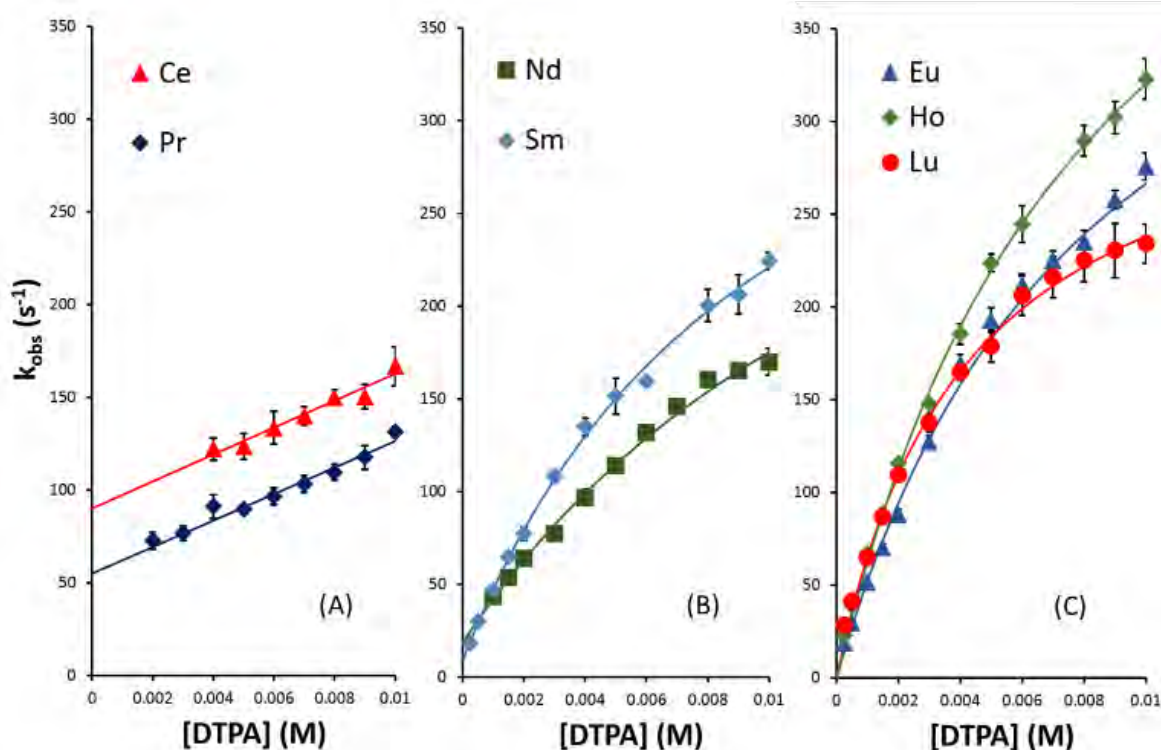


Fig. 3.3 – Dependence of the observed rate on the DTPA concentration for (A) Ce^{3+} and Pr^{3+} , (B) Nd^{3+} and Sm^{3+} , (C) Eu^{3+} , Ho^{3+} and Lu^{3+} in 0.4M total malonate solution, pH 2.5, $I = 1M$ at $25^{\circ}C$; $[Ln^{3+}] = [AAIII] = 10^{-5} M$. Lines represent the fits of the k_{obs} [DTPA] data.

Complex formation and dissociation reaction rate constants and pre-equilibrium constant determined by fitting k_{obs} – [DTPA] data for the lanthanides series at $25^{\circ}C$, pH 2.5, $I = 1M$ and $[Mal]_{tot} = 0.4 M$ are shown in Table 3.1.

Ln^{3+}	$k_d (\text{s}^{-1})$	$k_f (\times 10^3 \text{ M}^{-1} \cdot \text{s}^{-1})$	$K_{\text{pre-eq}} (\text{M}^{-1})$
Ce^{3+}	89.9 (5.5)	7.3 (0.8)	-
Pr^{3+}	54.6 (2.5)	7.2 (0.4)	-
Nd^{3+}	19 (5)	24.9 (3.5)	59 (19)
Sm^{3+}	9.1 (3.2)	42.2 (3)	99 (13)
Eu^{3+}	-	58.4 (4.3)	119 (19)
Gd^{3+}	-	62.7 (2.4)	89 (9)
Tb^{3+}	-	88.6 (3.3)	160 (12)
Dy^{3+}	-	95.9 (3)	230 (12)
Ho^{3+}	-	69.7 (1.9)	118 (7)
Er^{3+}	-	69.8 (2.9)	150 (12)
Tm^{3+}	-	82.5 (7.4)	213 (33)
Yb^{3+}	-	87.1 (4.7)	244 (22)
Lu^{3+}	-	81.1 (3.3)	241 (16)

Table 3.2 – Complex dissociation (k_d) and formation (k_f) rate constants and pre-equilibrium constant for the lanthanides series with DTPA (0.25 mM to 10 mM) in 0.4 M total malonate solution, at 25°C, pH 2.5, $I = 1 \text{ M}$. $[\text{Ln}] = [\text{AAlII}] = 10^{-5} \text{ M}$. Values in parentheses are the uncertainties at $\pm 1\sigma$.

pH dependence

The pH of the solution is an important parameter, since it will determine the degree of protonation of the DTPA and of the malonic acid; by extension, it also impacts the degree of complexation by either ligand. In the present work, the influence of the pH on the rate of the complexation of Eu^{3+} by DTPA has been investigated, in the range of pH = 2.1 to 3.1, for different total malonate concentrations. In this range of pH, according to the data available in the literature³³, malonic acid species are H_2Mal and HMal^- , the proportion of HMal^- varying from 15.7% to 64.8% from pH 2.1 to 3.1 and inversely for H_2Mal ; the proportion of Mal^{2-} is negligible at those pH values. Acidity of the solutions has also an important influence on the degree of protonation of DTPA, which decreases from an average 4.4 at pH 2.1 to 3.2 at pH 3.1. As an example, k_{obs} - $[\text{DTPA}]$ data are shown in Fig. 3.3 for Eu^{3+} in 0.4 M malonate solutions at different pH values. Experiments have also been conducted with Pr^{3+} at pH 2.5, 2.83 and 3.11 in 0.4 total malonate solutions at 25°C, $I = 1 \text{ M}$.

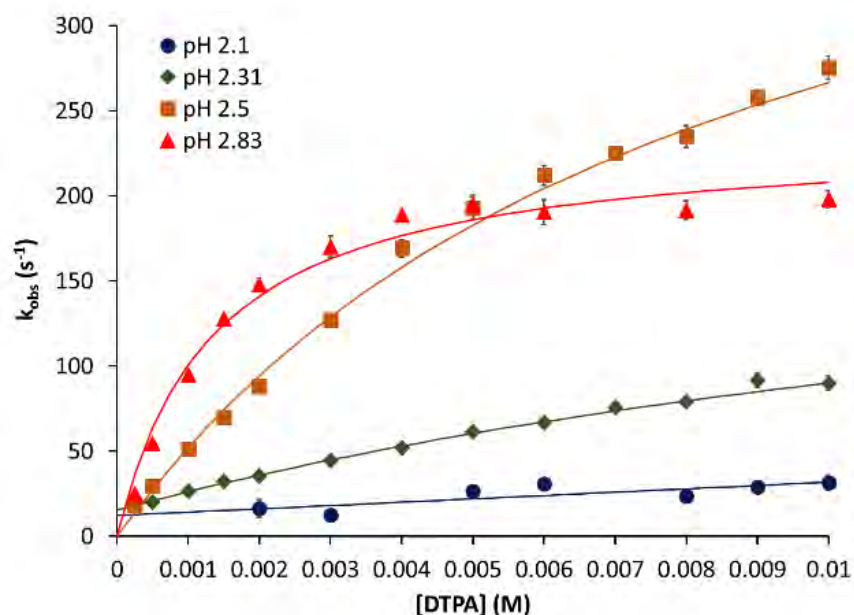


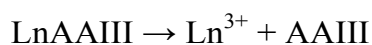
Fig. 3.4 – Dependence of observed reaction rate constant of Eu^{3+} on pH at 25°C and $[\text{Mal}]_{\text{tot}} = 0.4 \text{ M}$, $I = 1 \text{ M}$; $[\text{Eu}] = [\text{AAIII}] = 10^{-5} \text{ M}$. Lines represent the fits of the k_{obs} [DTPA] data.

Raising the pH of the solutions leads to an earlier occurrence of the saturation effect. It also increases the slope of the linear dependence of k_{obs} to [DTPA] for the lower DTPA concentrations. Using equation (1), the complex dissociation and formation constants and the pre-equilibrium constant have been determined and are shown in Table 3. The 1:1 Ln-DTPA complex formation constant (k_f) and the pre-equilibrium constant ($K_{\text{pre-eq}}$) increase with the pH while the dissociation constant decreases. This trend is opposite that observed in a previous study of La^{3+} complexation by DTPA in lactate buffer solutions¹³. The observation that has been made above that the total concentration of malonate has a minor influence on the rate constants (at pH 2.5) seems to be only valid at pH 2.5, as it is seen that at pH 2.1 and 2.83 the different constants vary for different total malonate concentrations.

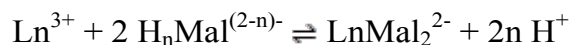
Mechanism

On the basis of the different results obtained in this study, the following mechanism is proposed as one of the possible and most probable way for the reaction of complexation of the heavy lanthanides by DTPA in malonate media to occur:

As the reaction begins, it is assumed that Arsenazo quickly released Ln^{3+} since Arsenazo has been proved to not alter the kinetics of the reaction.



Then, the lanthanide is rapidly complexed by the malonate ions present in solution. The more important concentration of malonate as well as the bidentate coordination mode of malonate with lanthanide against the octacoordinated DTPA makes the lanthanide interacting with malonate at first.



The positive entropy of activation suggesting a dissociative mechanism, the Ln-malonate complexes could be interacting with DTPA as illustrated in Fig. 13: as the DTPA is approaching the Ln-malonate complex, bond breaking occurs and malonate ions could become monodentate. It has been shown that the pre-equilibrium constant is only dependent on $[\text{HMal}^-]$, hence, the equilibrium between the malonate anions mono- and bidentate coordinated to Ln shown in Fig. 3.4 could correspond to the pre-equilibrium observed in the kinetics experiments. This pre-equilibrium, which occurs only for heavy lanthanides, could be due to stronger interaction between heavy lanthanides and malonate, while for light lanthanides those interactions would be not strong enough to form this complex.

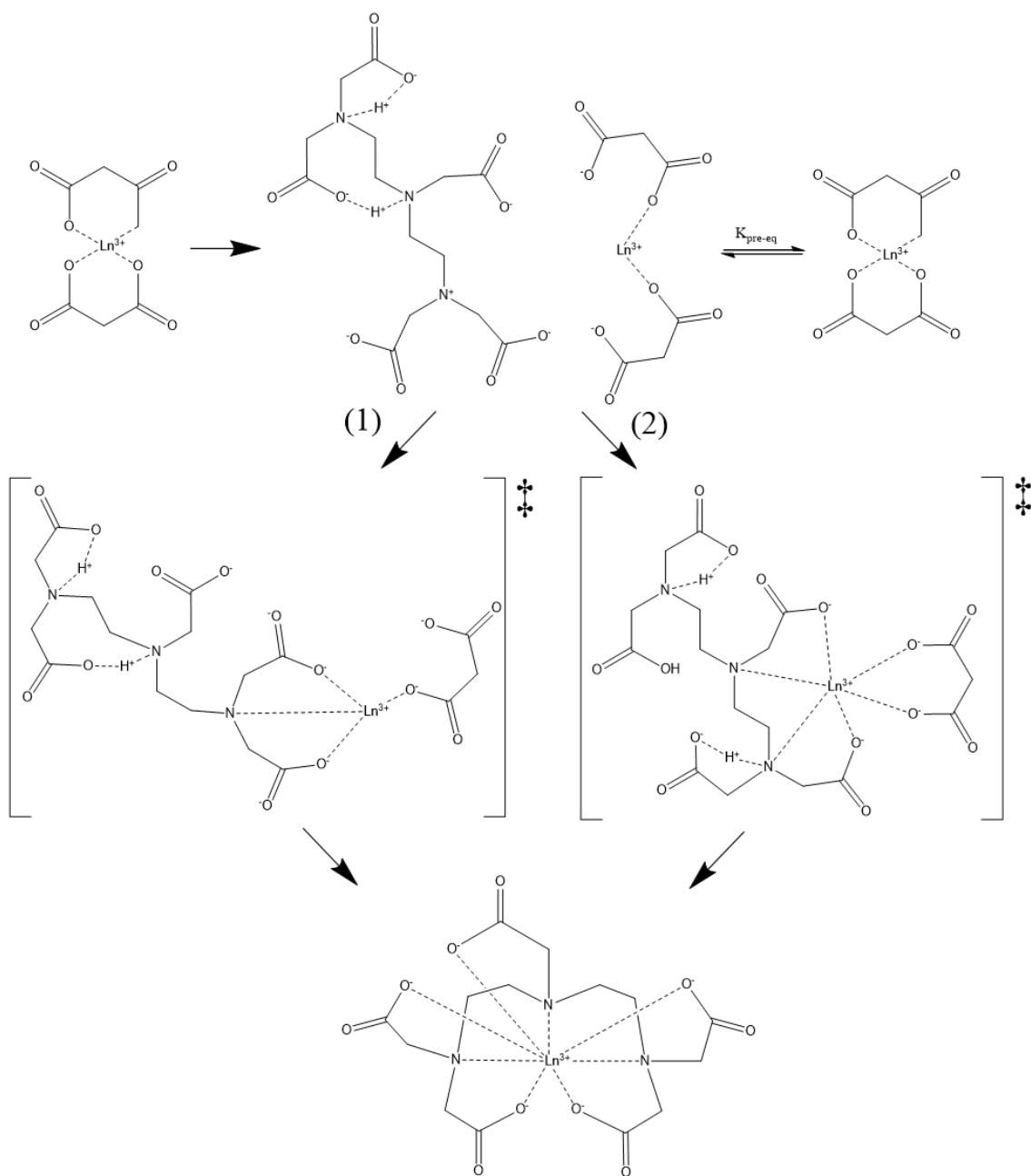


Fig. 3.4. – Illustration of possible pathways leading to the complexation of heavy lanthanides by DTPA in malonate media based on kinetics experiments analysis.

This first step is also coherent with the ionic strength dependence experiment, which shows that species of the same charge are interacting, i.e. in this case LnMal_2^{2-} and $\text{H}_2\text{DTPA}^{3-}$.

Then two pathways have to be considered:

- (1) DTPA is approaching the Ln-malonate complex already partially dissociated (one malonate has already left due to steric hindrance) by the diethylamine-di-acetate part of the DTPA molecule starting to form an eight-member ring. The lanthanide is voluntarily left closer to the malonate ligand considering that the bond order in the transition state is < 0.5 , which means that the transition state looks more alike the reactant than the product.
- (2) This second pathway corresponds to the approach of DTPA to the lanthanide by the triethyl-di-amine-di-acetate part of the DTPA molecule.

In this case, a larger eleven-member ring is formed; the coordination cage being more important, the malonate ion is believed to stay bidentate coordinated, or eventually the two malonate ions could be still both monodentate coordinated to the lanthanide, the steric hindrance being much less important than in the pathway (1). The pathway (2) is one of the possible ways, though the intermediate species exhibits more bond than the reacting Ln-malonate complex, which is unlikely considering a dissociative mechanism.

In the case of light lanthanides (Ce^{3+} and Pr^{3+}), due to weaker interactions between light lanthanides and malonate compared to heavy lanthanides, the pre-equilibrium does not occur, and malonate ions are believed to more easily broke bond with lanthanides and release the lanthanide while DTPA is approaching. This would explain while the observed rate constant k_{obs} varies linearly with the DTPA concentration.

Nd^{3+} and Sm^{3+} have an intermediate behaviour between light and heavy lanthanides, with both a k_d and K_{pre-eq} constant to fit the experimental data. This could mean that both mechanisms described above occur for those two lanthanides, due to intermediate interactions between those lanthanides and malonate ions, the strength of those interactions being progressive across the lanthanides series.

Another argument can be made concerning the difference between light and heavy lanthanides complexation pathway considering the ionic strength dependence. Heavy lanthanides exhibit a stronger dependence on the ionic strength, with a slope of 11.5 compared to a slope of 2 for light lanthanides. This difference could be explained by an additional local interaction between the negative charge of oxygen atoms of malonate and DTPA ions illustrated in Fig. 13 in addition to the two anionic species interaction. In the case of light lanthanides, if the malonates ions leave more easily, this interaction does not occur, and the ionic strength has less influence on the reaction rate. If this is what happens during the complexation process, then it would mean that the rate limiting step would be the breaking of bonds between the lanthanides and the malonate ions for both light and heavy lanthanides. This is consistent with the fact that malonate ions have to be involved in the rate limiting step, since the reaction is too fast to be measured by stopped-flow spectrophotometry in the absence of malonate.

Conclusion

Studying the complexation of lanthanides by DTPA in malonate buffered solutions allows the determination of the rate constants of the reaction at a time scale accessible by stopped-flow spectrophotometry. An auxiliary colored agent, Arsenazo III (AAIII), has been used to follow

the decrease of the absorbance of Ln-AAIII complexes while Ln-DTPA complexes are formed. The observed rate constant k_{obs} has shown a linear dependence to [DTPA] for light lanthanides (Ce^{3+} and Pr^{3+}), while a saturation effect is observed at high [DTPA] for heavy lanthanides (Eu^{3+} to Lu^{3+}), suggesting the formation of a precursor complex. Nd^{3+} and Sm^{3+} have an intermediate behaviour. It has been observed that k_f and K_{pre-eq} increase across the lanthanides series while k_d decreases at 25°C pH 2.5, $I = 1$ M, $[Mal]_{tot} = 0.4$ M. Linear Free Energy Relationships (LFERs) have been found between thermodynamic data from literature and kinetics data of this work, showing that the driving force of the reaction is the balance between the interactions of malonate and DTPA with lanthanides. The determination of the activation parameters has highlighted a dissociative mechanism, where Ln-Mal bonds break before DTPA complexes lanthanides. It also has been demonstrated that the intrinsic barrier mostly controlled the reaction kinetics, while the thermodynamic contribution could explained the difference between the lanthanides. The acid dependence experiments have allowed to develop arguments that H_2DTPA^{3-} and $Ln(Mal)_2^{2-}$ are the reacting species, which has been shown to be coherent with the ionic strength dependence experiments. Temperature studies have highlighted a dissociative mechanism due to positive entropy of activation. A mechanism involving different pathways coherent with all those observations has been proposed. The difference observed between light and heavy lanthanides could be explained by an increase of the strength of interaction between lanthanides and malonate ions across the lanthanides series.

Study of the kinetics of complexation of lanthanides by DTPA has been done in malonate media, which is a potential candidate to replace lactic acid buffer in TALSPEAK-like systems. A wider range of DTPA concentration has been investigated compared to earlier studies, showing a saturation effect under certain conditions. In order to develop a process, it is always interesting to find conditions where important parameters such as kinetics are constant, which could help modelling such processes.

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Accomplishments

- Primary goal of training very junior investigators was successful – second year graduate students operating independently.
- Some application of fluorescence spectroscopy to mixed extractant systems points toward predictable stoichiometry in extracted complexes, but some surprises as well.
- NMR dynamics studies establish that some features of lanthanide interactions with HEH[EHP] (extractant for Advanced TALSPEAK) are not very different from those of HDEHP (conventional TALSPEAK extractant) but unexpected magnitude of diluent effects on rates are a surprise.
- Stopped-flow kinetic results indicate rapid complexation kinetics for Ln-DTPA in 0.4 malonate buffer solutions
- Absorption spectrophotometry results suggest possible mixed HEDTA-malonate complexes in mixed media also supporting Advanced TALSPEAK malonate buffer option

One postdoc contributed four months of effort during FY 14, a second about 9 months, the third about nine months. The departed postdocs have found employment with Areva in France and as a postdoctoral associate at Argonne National Lab. The project also supplied partial support to a Sabbatical visitor in the winter quarter 2014.

Strategic Objectives to completion of the project (publications) Ultimately, our intent is that we will compare and contrast the results from these various complementary techniques/studies to provide a stronger basis for predicting the performance of extractant/diluent mixtures as media for metal ion separations. As many/most of these techniques require the presence of metal ions at elevated concentrations, these studies will ultimately take this investigation into the realm of patterns of supramolecular organization of metal complexes and extractants in concentrated aqueous/organic media. We expect advancements in the design of new solvent extraction procedures to be seen as a result of the application of fundamental chemical principles to explaining interactions in complex media.

With more than one fuel cycle separation project under active investigation, it is a challenge sometimes to establish “boundaries” between activities. It can also be argued that maintaining boundaries between complementary activities can sacrifice some of the value of large group interactions. Further, it is a matter of fundamental preparation for a career in research that young investigators be introduced to the

concept of “multitasking”. Graduate students are spared this additional complication; it is important that postdocs have such experiences. In this program, postdocs are also asked to assume leadership responsibilities, not as a substitute for the PI, but as a complement and surrogate. In this research program, the PI is always available for consultation and advice.

Summary of Task 1: Investigation of the dynamics of selected lanthanide ligand exchange with Advanced TALSPEAK/ALSEP extractant HEH[EHP] has produced fresh insights into organic phase reactions in these systems. Expected outcome for the post-completion period is the preparation of a manuscript comparable to previous HDEHP Dalton paper. The PI, Ms Krahn, and Dr. Marie have submitted a review of applications of NMR spectroscopy in solvent extraction of f-elements. A major focus for future directions will be on the effect of diluents and extractant concentration on the dynamics of acidic organophosphorus extractant exchange kinetics. As practical, these studies will address applications of ^{31}P NMR in mixed extractant and various diluent media. Though the interactions are complex and surprisingly variable, we strongly believe that these studies will ultimately produce significant advanced in separation science.

Summary of Task 2: with increasingly productive effort, significant progress has been made on application of titration calorimetry to the conventional TALSPEAK (lactate based) system, particularly as instrument difficulties, graduate student experimental maturity, and successful demonstration of an entropy titration has been accomplished, laying a foundation for future application of the methods. Calorimetry experiments on systems this complex are unusually challenging, perhaps justifying extra person-power. One long term objective of this task is to attempt application of the entropy titration concept to biphasic calorimetry, which was introduced (or perhaps re-invented) in this lab in the 2007-2010 time frame, but not advanced since due to the departure of the expert for INL. It is conceivable that some effort will be dedicated toward this task, with some investigation of the applicability of entropy titrations to the HEDTA-malonate system of Advanced TALSPEAK.

Summary of Task 3: The continuing objective of this task is to complete characterization of the Nd/Am complexes with malonate, HEDTA and the mixture of the two to determine whether or not mixed complexes are formed often in TALSPEAK-like systems (combining complexing buffers with actinide-selective complexants); a manuscript for publication is anticipated once issues of interpretation are resolved (to complement the one already in print). Likewise, the lanthanide-malonate-DTPA kinetics investigation should be matured to the point of publication soon; a manuscript for publication is anticipated. Further integration of FTIR and lanthanide/actinide fluorescence experiments into our program is already underway, addressing thus far characterization of other separation systems. This technique will ultimately prove valuable in the research objectives of each of these tasks. Possible targets for further investigations of fluorescence spectroscopy will grow out of our other NEUP project research, particularly those activities targeting the synthesis of new ligands, which is receiving a growing emphasis due to the willingness of new students to take on organic synthesis projects. Our investigations of diluent properties will likewise continue with a search for correlations between organic phase water content and interfacial tension, and a more detailed look at diluent effects and the effect of adding phase modifiers on the thermophysical properties of biphasic systems. Due to the exploratory nature of this latter focus, it is difficult to project publication plans at present.